AGENDA –Day 1

Tri-Service Ecological Risk Assessment Work Group
NAVBASE Ventura County – Port Hueneme, CA
NFESC, 1100 23rd Ave, 1st Floor Main Conference Room (A100/A101)
24-25 January 2006

Tuesday, 24 Jan 06 – Open to all

0800 – 0830	**Coffee and Donuts**
0830 - 0845	Welcome and Introductions – Ruth Owens, NFESC
0845 - 0930	Evaluation Of QSAR Models For Predicting Eco-Tox Behavior Of New Chemicals – Randy Cramer, NSWC Indian Head
0930 –1030	Chemical Bioavailability Assessments for Soil and Sediments – Joe Kreitinger, RETEC
1030 - 1045	**Break**
1045-1130	Comparative toxicity of 2,4 and 2,6-DNT in Northern bobwhite – Dr. Michael Quinn, CHPPM
1130 – 1245	**Lunch**
1245 – 1330	Uncertainty And Variability In Publicly Available Log Kow Data: Sources And Consequences – Dr. Igor Linkov, Cambridge Environmental Inc
1330 - 1415	Use of Computational Chemistry to Address Emerging Contaminants – Dr. Leonid Gorb, ERDC
1415 – 1430	**Break**
1430 - 1515	Approaches to Prioritization of Materials of Evolving Regulatory Interest (MERIT) - Dr. Igor Linkov, Cambridge Environmental Inc
1515-1615	New Models for Predicting Indoor Vapor Concentrations for Buildings with Crawl Spaces & Basements: Case Study and Future Directions – Dr. Mark Rigby, TetraTech
1615-1645	Napthalene – Bioassays and Regulatory Implications – John Hinz, AFIOH/RSRE
1645 – 1700	Wrap-up
1800 - ????	Happy Hour and Dinner

AGENDA –Day 2

Tri-Service Ecological Risk Assessment Work Group

NAVBASE Ventura County, Port Hueneme, CA
Public Works Department, BLDG 850, Main Conf Rm
24-25 January 2006

Wednesday, 25 Jan 06 – DoD Only

0830 - 0900 Coffee and Socializing

0900 - 0915 Brief Welcome and Selection of new Workgroup Lead – Andy Anders

0915 - 1000 Emerging Contaminants: Strategic Priorities & Action Plan – Paul Yaroschak, OSD

1000 - 1030 DoD's Various Levels of Concern - State of the Practice - Drew Rak, Mitretek

1030 – 1045 Break

1045 - 1115 R3 (Risk Assessment, Management and Communication) Workshop Discussion

1115 - 1130 Army Update – Laurie Haines, others

1130 -1145 Navy Update – Ruth Owens

1145 - 1200 Air Force Update – Andy Anders

1200 – 1230 Working Lunch-Sandwiches Brought in

1230 - 1345 Purplization of Various Guidance Documents – Discussion – Mark Johnson

- Development of Terrestrial Exposure and Bioaccumulation Information (and new appendices; Army) - Johnson
- Kriging in Eco-Risk Assessments (Navy) - Johnson
- Laboratory Detection and Reporting Limits Issues Related to Risk Assessments (Navy) - Anders
- Guidelines for Evaluating Existing Analytical Data to Determine Suitability for Use in ERAs (Navy) - Anders
- Rapid Sediment Characterization (RSC) Tools for ERAs (Navy) - Suedel-Steevens
- Using Monte Carlo Analysis in ERAs (Navy) - Anders
- Reviewing ERA Deliverables (Navy) - Gaizick
- Ecological Risk Assessment Standard Deliverables (Navy) - Gaizick
- Technical Document for Ecological Risk Assessment: Planning for Data Collection (Army) - TBD
- Process for Developing Management Goals for ERAs (Army) - TBD
- Selection of Assessment and Measurement Endpoints for ERAs (Army) - TBD
- A Guide to Screening Level Ecological Risk Assessment (Army) - TBD

1345– 1400 Topics for Next Meeting
Recapping Action Items
Schedule Next Meeting

ISSUE PAPER

Key Risk Assessment/Risk Management Issues

Executive Issues:

- There is a need to improve the science, timeliness of information, stakeholder collaboration, and transparency related to the risk assessment/risk management process for emerging contaminants. Resources need to be focused on highest priority needs. Thus, how can federal and state capacities be enhanced through collaborative efforts?
- Prior to published regulatory standards and/or vetted health risk information (e.g., RfDs), what conditions, considerations or criteria should trigger the expenditure of funds (and by whom) for such actions as sampling or interruption of exposure pathways?

Background:

Chemicals entering society and the regulatory sphere

- There are hundreds of new chemicals and materials introduced into society every year as well as thousands of older chemicals in use.
- The Toxic Substances Control Act (TSCA) gives EPA the ability to track industrial chemicals currently *produced or imported* into the United States. EPA repeatedly screens these chemicals and can require reporting or testing of those that may pose an environmental or human-health hazard. EPA can ban the manufacture and import of chemicals that pose an unreasonable risk.
- EPA classifies chemical substances as either "existing" chemicals or "new" chemicals. Any substance that is not on EPA's Toxic Substances Control Act Chemical Substance Inventory (commonly referred to as the TSCA Inventory) is classified as a new chemical. There are approximately 75,000 chemical substances on the Inventory at this time but the Inventory does not capture all the chemicals in use.
- A new chemical is eligible for addition to the TSCA Inventory after specific notices/forms are submitted to EPA for review. After review by EPA, the chemical will be listed. Once a substance is listed on the TSCA Inventory, it is considered an existing chemical.
- At the time chemicals are added to the TSCA inventory, the extent and scope of toxicological information on these chemicals varies and may not be sufficient to assess risk to human health.
- A number of other laws (e.g., Clean Water Act, Clean Air Act) *control the release* into the environment of specific chemicals.
- Yet other laws dictate response actions for *uncontrolled releases*. For example, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) establishes requirements for response to releases of "hazardous substances" and "pollutants and contaminants". The Resource Conservation and Recovery Act has similar requirements.

Assessing Risk

- Risk assessment is the process by which the form, dimension, and characteristics of risk to human health and the environment are estimated.
- Epidemiological and toxicological studies on chemicals are performed by a wide variety of government, academic, and private entities, with a varying quality controls. Peer review seeks to

ensure sufficient rigor in scientific procedures such that the results of the study can be used to help assess risk.

- EPA has gathered information and conducted research on a subset of the total universe of chemicals in use. This information is maintained in several programs and databases including the Integrated Risk Information System (IRIS), the Toxic Release Inventory (TRI), and those in the Office of Pesticide Programs, and the Office of Water.
- Other agencies (e.g., Agency for Toxic Substances and Disease Registry) also collect information and conduct research on new and existing chemicals and compounds.
- For risk values related to remediation, EPA and many states/federal agencies follow the recommended EPA toxicity value hierarchy:

  1. Integrated Risk Information System (IRIS) and cited references. Changes are made in this database as new chemicals or chemical information becomes available, but there may be data gaps.

  2. The Provisional Peer Reviewed Toxicity Values (PPRTV) and cited references developed for the EPA Office of Superfund Remediation and Technology Innovation (OSRTI) programs.

  3. Other toxicity values such as:

     - California Environmental Protection Agency toxicity values, available on Cal-EPA's website.
     - The Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Levels (MRLs), addressing non-cancer effects only, available on ATSDR's website
     - The EPA Superfund Health Effects Assessment Summary Tables (HEAST) database and cited references.

Managing Risk

- Risk management is the process by which risk is reduced, ideally to acceptable levels.
- Under CERCLA, the President is authorized to take response actions, consistent with National Contingency Plan, whenever there is a release or substantial threat of a release of hazardous substances <u>or</u> a release or substantial threat of a release of any "pollutant or contaminant" which may present an imminent and substantial danger to public health or welfare.
- CERCLA response actions are risk-based in accordance with the National Oil and Hazardous Substances Spill Contingency Plan regulations. State response action requirements are also usually risk-based.
- There are a number of other laws (e.g., Safe Drinking Water Act), that authorize regulatory agencies to take action, or require others to take action, when there is a threat to human health.
- Many of legal/regulatory requirements are based on specific emission limits (e.g., NPDES permits), which consider risk and cost/benefit among other factors.

<u>Discussion:</u>

- Given the above background, federal and state officials, especially field personnel, are presented with a number of challenges *regarding emerging contaminants*.
- IRIS has data gaps and sometimes lacks currency related to studies and data entered into IRIS.
- Toxicological and epidemiological information is somewhat scattered among a number of databases and sources.
- Risk assessors often find it difficult to derive risk values and resolve technical risk assessment issues with limited staff/resources and with limited/scattered health risk information.

- Regulators find it difficult to respond to public concerns or require actions from responsible parties when there is limited health risk information.
- Responsible parties find it difficult to secure funding for response actions when there is limited health risk information and/or no published standards.

Recommendations:

- Develop a collaborative federal-state process to identify contaminants of most concern, identify gaps in science related to human health risk, prioritize additional research needs, and make available a common database of information. The process will seek to leverage state and federal resources, coordinate activities to avoid duplication and focus available resources on areas of greatest potential risk.

- Develop a protocol, decision chart, or criteria to be used by risk management officials to help determine appropriate response actions for ECs. Criteria may be different depending on whether the EC is new, being reassessed or can be detected at new levels. The protocol will provide logic and justification for EC response actions for budgeting purposes.

WORKING DEFINITION

Emerging contaminants are chemicals or materials:

That have:

- A perceived or real threat to human health or environment
- Evolving regulatory interest
- No published health standard, or an evolving standard

And may have:

- Insufficient human health data/science
- New detection limits
- New pathways

TSERAWG
JAN 24

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NAPHTHALENE
BIOASSAYS & REGULATORY IMPLICATIONS

The Model & Meaning To AFIOH & USAF Of Naphthalene's Reassessment As A Potent Carcinogen

JOHN P. HINZ
Health Risk Assessment Branch
Air Force Institute for Operational Health
Brooks City-Base, TX

TSERAWG - Port Hueneme
(Jan06)

OUTLINE

- Background On Naphthalene
  - What Started All The Fuss?
- How is It Important To AF & DOD?
- Is It's Cancer Designation Significant?
  - Regulatory, Economic & ESOH Impacts
- Other Perspectives
  - Epidemiologic Perspective
  - DOT's Perspective
  - Industry's Perspective
  - An ERPIMS Perspective
- The model of more to come…?

WHAT STARTED ALL THE FUSS?

EPA Targeted Naphthalene - Significant Events

- Cancer Assessment:
  - NTP rat bioassay (2000) -> cancer in olfactory epithelium
    "reasonably anticipated to be a human carcinogen"
  - EPA fast-tracked naphthalene's re-examination
    Expedited review targeting Dec04 release
    Earns critique on both process and substance from DOD & industry
  - DOD & industry questions reach OMB & WH
    Release postponed – EPA frustrated
  - Interagency controversy continues, Jan-Jul05
    Other agencies engaged
    OMB tasked DOD to "justify" concerns – answered Jul05
- Jul/Aug05:
  - Expose - Series of 5 "Inside EPA" articles

BACKGROUND

What is Naphthalene?

- Chemical Profile

A colorless-white solid of modest volatility that sublimes slowly at room temperature – moth balls.

A polyaromatic hydrocarbon and a natural constituent of petroleum products – fuels, lubes, asphalts.

Formula	C10-H8
Molecular Wt	128
MP & BP	80.2° C & 217.9° C
Odor Threshold	0.3 ppm (LOA = n/a)
Vapor Pressure	**0.085 mmHg (sat vap = 112 ppm)**
Solubility	**31 mg/L (water)**
LEL - UEL	0.9 - 5.9%

BACKGROUND
What is Naphthalene?

- Sources
  fossil fuel exhaust, cigarette smoke, wood burning, asphalts & sealants, pesticide, some fruits/vegetables, shellfish, BBQ meats smoked foods, breast milk
- Industrial production & use
  Production – petroleum cracking, coal tar distillation
  Uses – feedstock for phthalate anhydrides (phthalates) and other plasticizers, azo-dyes, carbaryl, creosote constituent, octane improver
- Ingestion & metabolism & effects
  Absorbed through all routes
  Metabolized via cytochrome P450 - ~30 metabolites identified
  Acute – hemolytic anemia
  Systemic – nausea/vomiting; CNS, kidney, liver effects, coma

BACKGROUND
What Started All The Fuss?

- Two Important NTP Bioassays Started All The Fuss!
  - Mouse 2-Year Bioassay (1992)
    - Route: inhalation
    - Exposure Levels: 0, 10, 30 ppm
    - Results: cytotoxicity w modest incidence of lung neoplasia of uncertain relevance; no nasal neoplasia

  → **Rat 2-Year Bioassay (2000)**
    - **Route: inhalation**
    - **Exposure levels: 0, 10, 30, 60 ppm**
    - → **Significant Results: cytotoxicity w unusual neoplasia in nasal olfactory epithelium**

BACKGROUND

Naphthalene Occupational & Regulatory Guidelines*

* [Non-cancer reassessment also under way]

ACGIH	10 ppm (STEL=15)
NIOSH	10 ppm (STEL=15; IDLH=250)
OSHA	10 ppm
AIHA (WEEL & ERPG)	n/a
NAC-AEGL (AEGLs)	n/a
EU (SCOEL)	"not feasible" (NTP & other bioassays)

EPA (drinking water)	0.1 – 0.7	mg/L
EPA (non-cancer)	0.02	mg/kg/D (RfD – lifetime)
	0.003	mg/m^3 (RfC – lifetime)
EPA (cancer – inh)	**0.0000107 mg/m^3 (2 ppt)****	

****de minimus**

IS NAPHTHALENE IMPORTANT TO AF & DOD?

It Might Brand Our Fuels As Carcinogens!

- CHANGE TO JP-8 FROM JP-4 (1996)
  - Safety & logistics
- THE UNIVERSAL FUEL
  - Airplanes, helicopters, tanks, trucks, space heaters, stoves, generators, dust suppression ... coolant ...
  - Kerosene + additives = commercial Jet-A & JP-8
- ANNUAL CONSUMPTION

  USAF -> DoD -> Civ Av -> USA -> World Wide

  2.5 -> 5.5 -> 25 -> 30 -> 60

  - BILLIONS OF GALLONS –
- **29CFR 1910.1000: If carcinogen content =/> 0.1%, the mixture considered carcinogenic**

  Crude oil >/=0.1% Gasoline 0-5%

  Jet fuel 1-3% Additives & blends </=10%

IS THE CANCER DESIGNATION SIGNIFICANT?
REGULATORY & ECONOMIC IMPACT

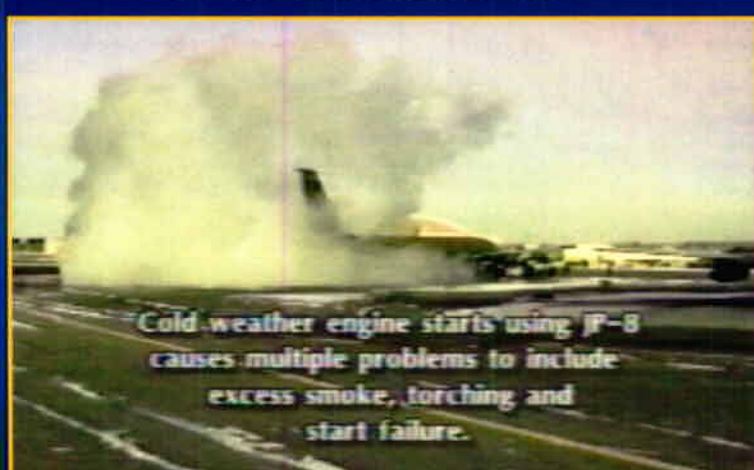
- OMB guidance on regulatory impact
  $100M = "significant"
  $500M = "highly significant"
- Price impact to remove naphthalene from jet fuel?
  - take benzene out of gasoline: 2-5 ¢/gal [per API]
  - take naphthalene out of jet fuel: 15-50% increase [per API]

• $1.80/gal [base price]	27 ¢/gal	90 ¢/gal
• AF uses ~ 2.5 **B** gals →	$ 675 M	$ 2250 M
• DOD uses ~ 5.5 **B** gals →	$ 1485 M	$ 4950 M
• USA uses ~30 **B** gals →	$ 8100 M	$ 27000 M

- **Naphthalene – "highly significant"**

IS THE CANCER DESIGNATION SIGNIFICANT?
ESOH IMPACTS

KC-135 Cold Weather Start

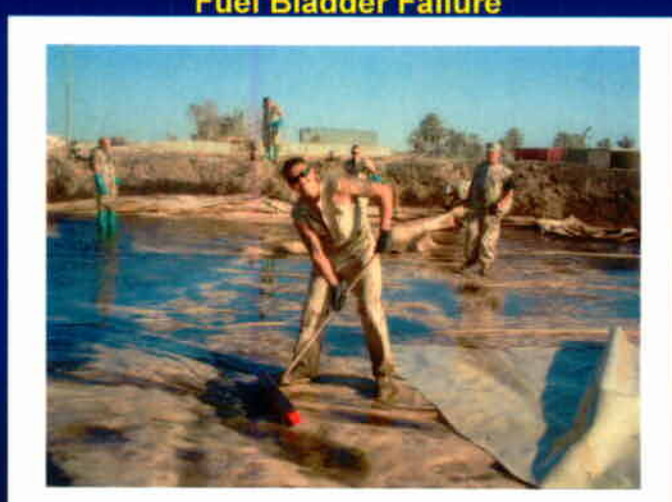


IS THE CANCER DESIGNATION SIGNIFICANT?
ESOH IMPACTS

Aircraft Service Operations
- confined space entry & exposure -

IS THE CANCER DESIGNATION SIGNIFICANT?
ESOH IMPACTS

Fuel Bladder Failure



IS THE CANCER DESIGNATION SIGNIFICANT?
ESOH IMPACTS

- Environmental Restoration
  - Cleanup of 1000 sites w fuel at issue - cancer risk not addressed
  - ~50% AF sites w fuel contamination - common analyte at AF sites
  - ***Records Of Decision may reopen for review***
- Safety & Operational Health Issues
  - Impacts on storage, transport, handling, use
  - Base-level occupational health programs affected
    - personnel training, engineering controls, PPE, monitoring air levels, medical surveillance, establishment regulated/restricted areas
  - ***Legacy issues from past exposures…***
- Costs – no estimates, assumed to be large

EPIDEMIOLOGIC PERSPECTIVE
Where are the bodies?

- No studies assess the association between naphthalene exposure & cancer
  - <u>Preliminary</u> assessment: exploit existing dataset of cancer vs occupation
- Jet fuel exposure vs invasive cancer in AF population
  - AF cases vs controls w >/= 1 duty, Jan88-Dec03
  - Exposure based on job description/classification (H / M vs L)
- Preliminary results:
  - Jet fuel exposure ***not*** significantly associated w invasive cancer
  - Odds Ratios for H & M < 1.0
  - Data adjusted for rank & marital status – no other confounders
  - "Healthy Worker Effect"?
    - USAF vs USA: AF healthier, diagnosed earlier

Adapted from Yamane & D'Mello
(AFIOH Epidemiology Branch)

OTHER PERSPECTIVES
USDOT - EMISSIONS COMPLIANCE

- EPA's *de minimus* risk estimate **2 ppt**
- Naphthalene in Cal So. Coast Air Basin ~1720 Kg/D
  Various sources – concentrations for LA air shed **~120 ppt**
- Most urban areas appear to range **~50-100 ppt**
- Chicago O'Hare metropolitan area
  Similar conc range w seasonal and diurnal variations
- National Air Toxics Assessment
  Air toxics inventory on ZIP code basis - N a regional risk driver
- Linking Inhalation Toxicity & Soil/Water Cleanup
  California EPA: route-to-route extrapolation to calculate ingestion rates – soil/water cleanup
- **Can *any* major metropolitan area meet this standard ?**

Adapted from Dr. David Belluck

INDUSTRY PERSPECTIVE - SUMMARY

Issue

- **EPA drafted overly conservative risk assessment for naphthalene**
  - Driven by observation of rare nasal tumors in rats
  - Naphthalene now considered a likely human carcinogen by EPA

Impact

- **Unit risk (0.01 per µg/m^3) -> 1E-6 *de minimus* air concentration of 2 ppt**
- **Naphthalene likely to become a new risk-driving constituent for air pollution**

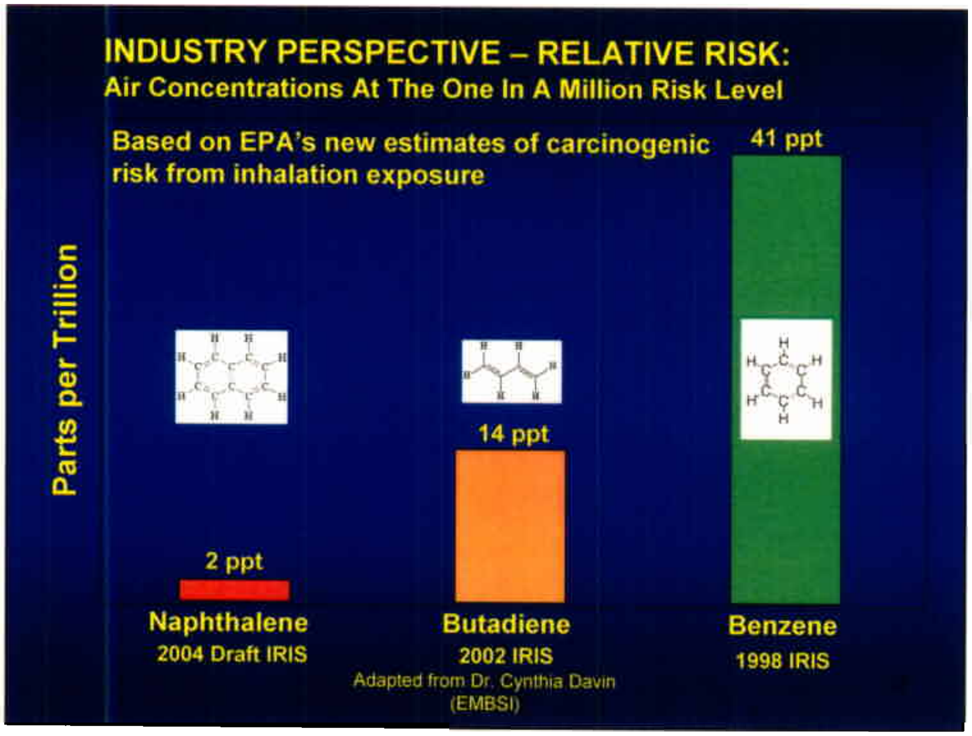
Analysis

- **Relevance of the rodent cancer data to human risk assessment is questionable**
- **Science does not justify conclusion that naphthalene is a potent human carcinogen**
- **EPA excluded significant stakeholder input**
- **EPA assessment is inconsistent with IARC, EU assessments**

Industry Approach

- **Build consensus between industry, academia, government about naphthalene's state-of-the-science, data gaps and research needs - Naphthalene Symposium**

Adapted from Dr. Cynthia Davin
(EMBSI)



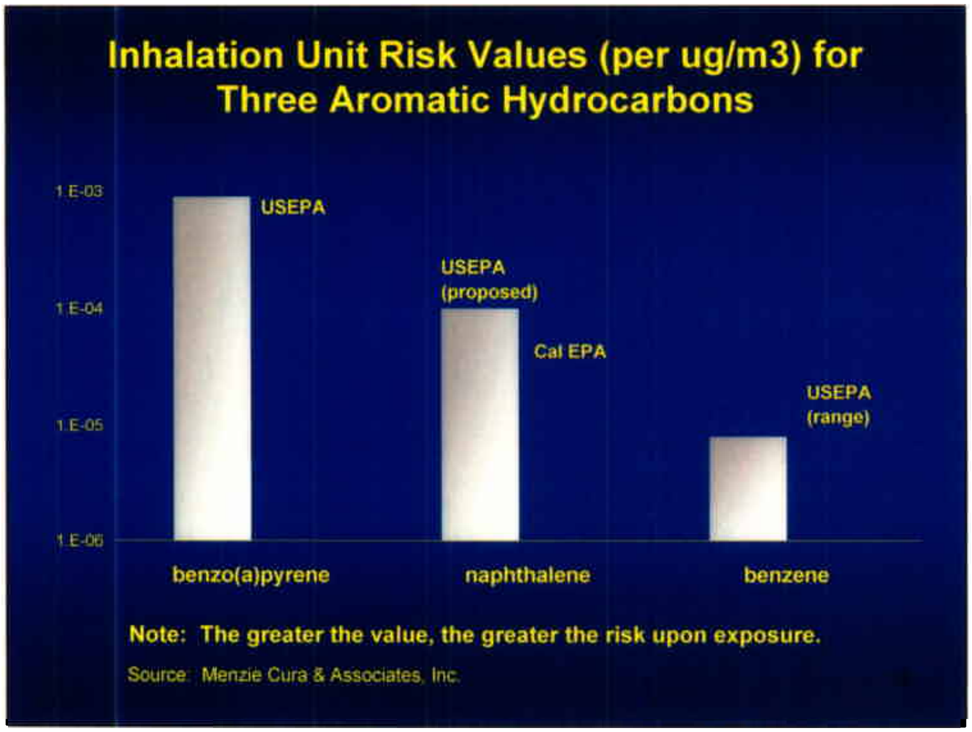
INDUSTRY PERSPECTIVE – ANOTHER VIEW
Status of Naphthalene

- NTP: Lists Naphthalene in 11th Report on Carcinogens
  "reasonably anticipated to be a human carcinogen"
- EPA - In Progress
  IRIS targets N for re-assessment - inhalation risk values under review
  CalEPA already developing/applying URV, cancer slope, NSRL

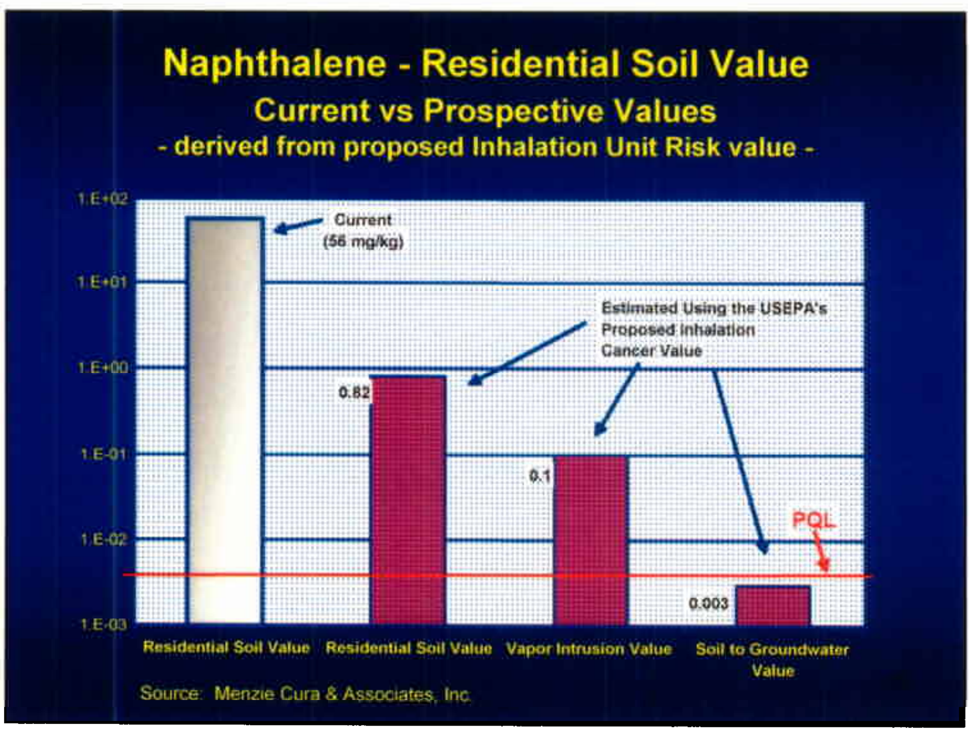
- IARC: Review Completed in 2002
  2B (*possibly carcinogenic to humans*) - NTP results **may not be relevant**
- EU: Naphthalene risk assessment published 2003
  Category 3 - substances which cause concern for humans … possible carcinogenic effects but … information is *not adequate*. *Some evidence* from animal studies but *insufficient* to place the substance in ***Category 2***.

- **Concern**
  Once promulgated, revised values (*even drafts*) will be used by EPA regions, other federal agency, and many state agency risk-based programs

Adapted from Dr. Anne LeHuray
(ACC)

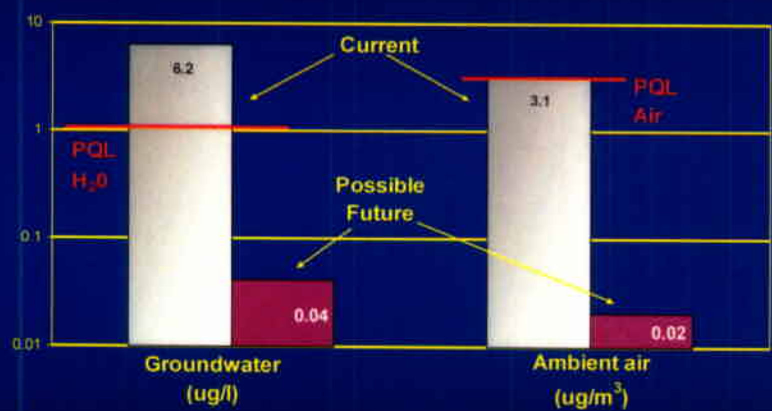


Inhalation Unit Risk Values (per ug/m3) for Three Aromatic Hydrocarbons
1.E-03
1.E-04
1.E-05
1.E-06
USEPA
USEPA (proposed)
Cal EPA
USEPA (range)
benzo(a)pyrene
naphthalene
benzene
Note: The greater the value, the greater the risk upon exposure.
Source: Menzie Cura & Associates, Inc.



Naphthalene - Residential Soil Value
Current vs Prospective Values
- derived from proposed Inhalation Unit Risk value -
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
Current (56 mg/kg)
Estimated Using the USEPA's Proposed Inhalation Cancer Value
0.82
0.1
0.003
PQL
Residential Soil Value
Residential Soil Value
Vapor Intrusion Value
Soil to Groundwater Value
Source: Menzie Cura & Associates, Inc.

Possible Changes to Groundwater (ug/L) and Ambient Air (ug/m3) Values



Note: Values are based on USEPA proposed IUR and Inhalation exposures.

Source: Menzie Cura & Associates, Inc

ENVIRONMENTAL PERSPECTIVE
ACFEE's ERPIMS & Naphthalene

Where do we find naphthalene?

- AFCEE's ERPIMS:
  - Rich data source w ~45M analytical records
  - Percent of samples w detects:
    groundwater, 63%; soil, 33%; sediment, 2%; surface water, 2%
    common sites – underground tanks & pipelines, landfills, spills
  - Most AF bases detect naphthalene
    individual sampling points, not commonly found

Can we measure it?

- Most bases exceed proposed criteria for soil & water
- Current analytical methods probably OK for soil: 820 ug/kg
- Current methods not sensitive enough for water: 0.04 ug/L

Adapted from Mr. Philip Hunter
(USAFCEE - ERPIMS)

IS NAPHTHALENE IMPORTANT TO AF & DOD?
It's The First Of Many Still To Come!

- 9Feb04: EPA-IRIS targeted **89** chemicals for attention
  - List includes naphthalene, 1,4-dioxane, AF ECs
- Question:
  - a) how many of the 89 concern us?
  - b) how do we address the growing RA problem?
  - Naphthalene – targeted first; something to learn from
- Cross-matched IRIS w 3 databases used by DOD
  - Out of the IRIS **89**
    - **81** – 91% – in HMIRS
    - **51** – 57% – in ERPIMS
    - **43** – 48% – in ATSDR's NPL list
      - **40** of these also in HMIRS
- **Importance to the AF**
  - **Naphthalene – model for 80 more assessments still to come**

New Models for Predicting Indoor Vapor Concentrations for Buildings with Crawl Spaces & Basements: A Case Study from Moffet Field

Mark C. Rigby, Bill Mills, Sally Liu, David Brenner[1], Sandy Olliges[2], and Thomas H. Anderson[2]

Tetra Tech [1]Neptune and Company, [2]NASA Ames Research Center

Indoor Vapor Intrusion

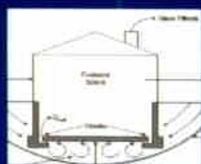
- Inhalation of vapors in indoor air is primary issue driving remediation at VOC sites
- Risks are generally much higher than
  - outdoor air inhalation
  - soil ingestion
- One accepted regulatory model:
  - Johnson and Ettinger model (USEPA 2004)

Johnson and Ettinger Model

- Model makes explicit assumptions
  - Cement foundation
    - Slab-on-grade
    - Concrete basement
  - Outdoor air is clean
  - Indoor air is well-mixed

Johnson and Ettinger Model

- Johnson and Ettinger model
  - Subsurface vapors migrate through foundation
  - Entry is via cracks in the foundation or the space between the foundation and the footer



  - Implication: the foundation acts as a vapor barrier

Crawl Spaces

- In the Western US, approximately 30% of houses have crawl spaces with dirt floors
- Two different types of crawl spaces:
  - Open:

  - Closed:

Crawl Spaces

- Crawl spaces provide potential for additional dilution from indoor-outdoor air exchange
- Crawl spaces have dirt floors so have no physical barrier to vapor intrusion (such as cement foundation)

- Conclusion - It is difficult to predict the effect of crawl spaces on vapor migration

Modeling Crawl Spaces

- Is J&E accurate?
  - Single compartment model
- Only one published model specifically incorporates crawl spaces
  - Turczynowicz and Robinson (2001)
  - 2 compartment model (dwelling and crawl spaces)
  - Model provides equations to estimate risks for residents (equations are in Laplace space)
  - Assumes soil source
  - Migration through bare earth floor instead of through cracks in cement foundation

Modeling Crawl Spaces

- We modified Turczynowicz and Robinson (2001) model to:
  - Predict crawl space and/or basement, and dwelling space vapor concentrations
  - Use groundwater source
  - Simulate either constant or diminishing groundwater source
  - Added porous media model to calculate Q_{soil}
- Model assumes
  - Bare earth floor in crawl space and cement floor in basement
  - Enclosed crawl space and/or basement with ventilation

Model Comparison

Feature	J&E	J&E-modified	VTM
Ambient air?	No	Yes	Yes
Basement crawl space combination?	No	Yes	Yes
Time variable?	No	No	Yes
Perimeter crack module for Q_{soil}?	Yes	Yes	Yes
Porous media model for Q_{soil}?	No	Yes	Yes
Diffusive transport?	Yes	Yes	Yes
Deep advective transport?	No	No	Yes
Solution technique	Three simultaneous linear equations	Five simultaneous linear equations	Numerically inverted Laplace transforms

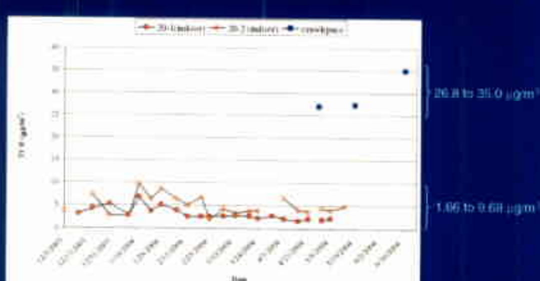
J&E Assumptions

- Will examine several assumptions with case studies
  - Cement foundation (no crawl space)
  - Outdoor air is clean
  - Indoor air is well-mixed

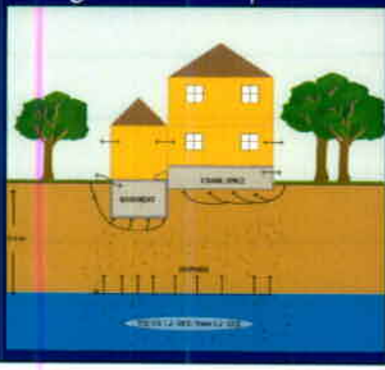
Crawl Space Case Study

- Moffett Field (CA)
- TCE, cis-1,2,DCE, and trans-1,2-DCE groundwater plume underneath
  - Concentrations decreasing over time
- Measured indoor air concentrations for several buildings
  - 1 building with a crawl space (Building 20)
    - Not used/uninhabited
  - Indoor air measured on Dec. 2003 - April 2004
  - Crawl space air measured April - June 2004

Measured Air Concentrations

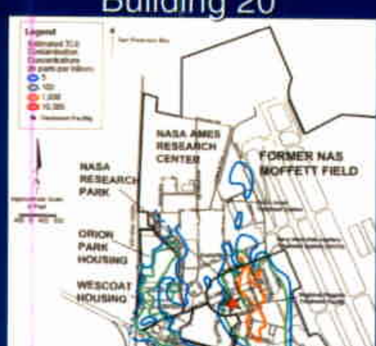


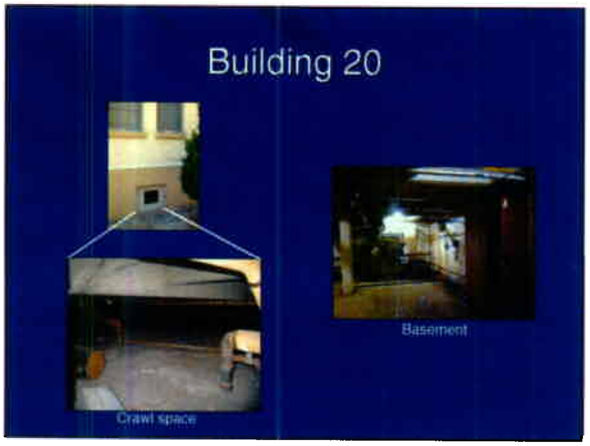
Building 20 Conceptual Model



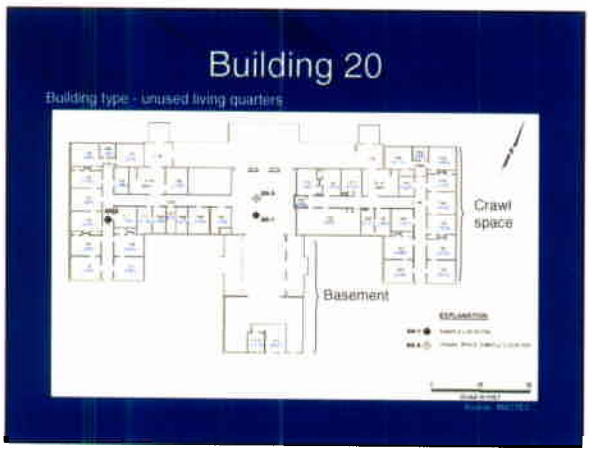
Building 20

Building 20

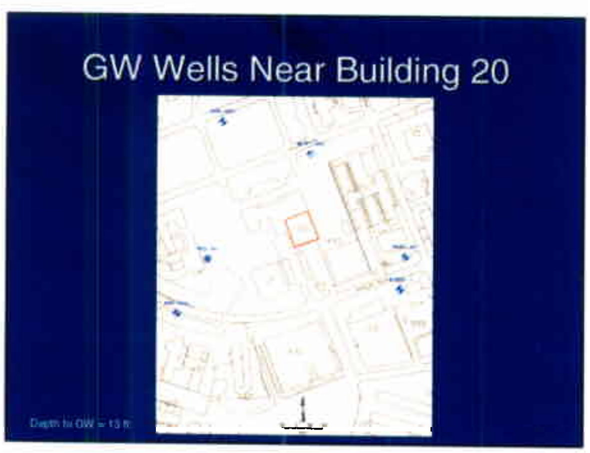




Building 20
Basement
Crawl space

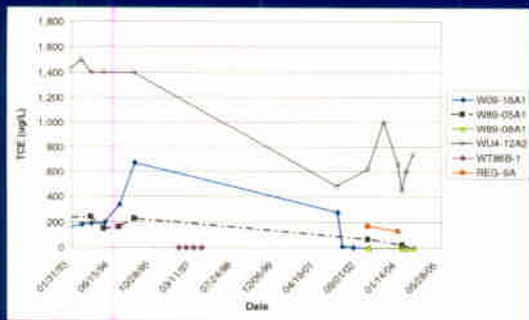


Building 20
Building type - unused living quarters
Crawl space
Basement



GW Wells Near Building 20
Depth to GW = 13 ft

GW Wells Near Building 20



Model Input Data I

- Set up three different models
  - Standard J&E slab-on-grade
  - J&E-modified
  - VTM
- Building volume: 183,800 cu.ft.
  - Since building was irregular shape with uneven ceilings, used plans to estimate volume
    - 163,000 cu.ft. for the two storey portion
    - 20,800 cu.ft. for the one storey portion
- Air exchange rate: 0.2 ACH
  - 10th percentile in western region (USEPA 1997)
- Soil physical properties: Silty clay

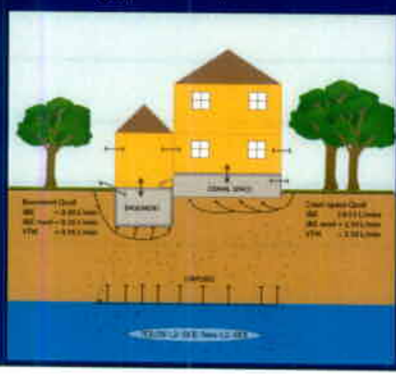
Model Input Data II

- Depth to GW (site specific): 13 feet
- Concentrations in GW:
  - TCE: 200 µg/L
  - cis-1,2-DCE: 25 µg/L
  - trans-1,2-DCE: 0.6 µg/L
- Concentrations in outdoor air:
  - TCE: 0.08 µg/m^3
  - cis-1,2-DCE: 0.04 µg/m^3
  - trans-1,2-DCE: 0.01 µg/m^3
- ΔP = 2 Pa (VOLASOIL default for buildings with crawlspaces)

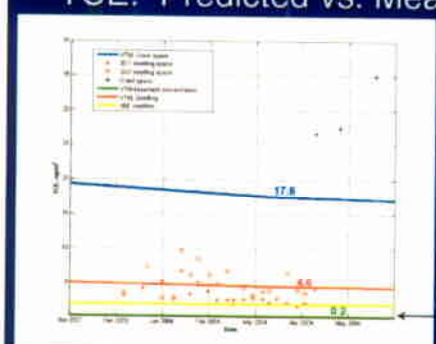
Crawl Space/Basement Model Data

- Crawl space parameters
  - Height: 30 inches
  - Crawl space/outdoor exchange rate: 0.2 ACH
  - Crawl space/indoor exchange rate: 0.03 ACH
- Basement parameters
  - Height: 6 feet
  - Basement/outdoor exchange rate: 0.2 ACH
  - Basement/indoor exchange rate: 0.02 ACH
- Basement/crawl space exch. rate: 0 ACH

Q_{soil} Comparison



TCE: Predicted vs. Measured

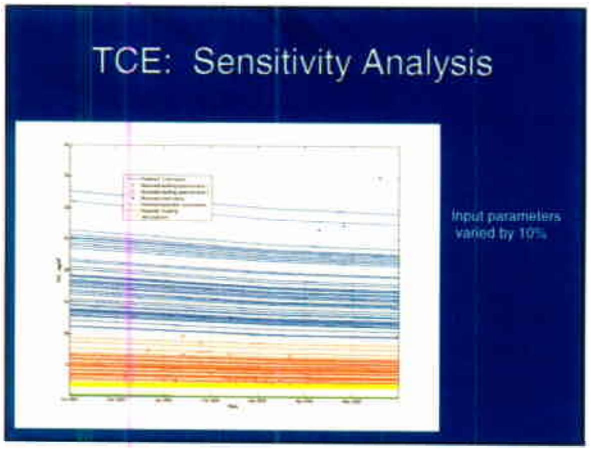


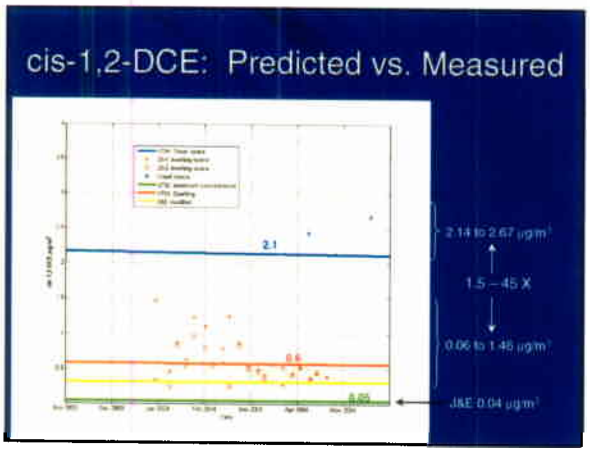
26.8 to 35.0 µg/m³

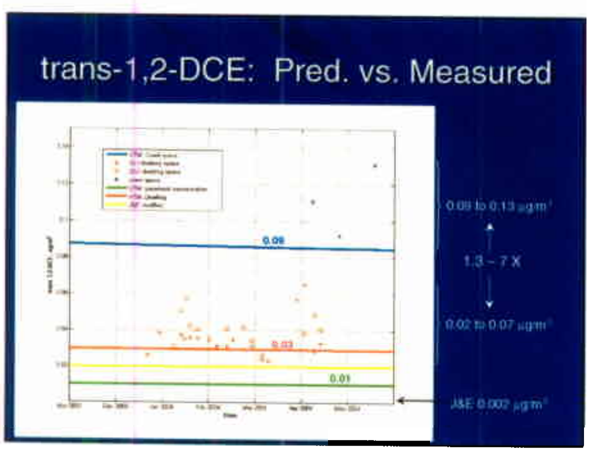
3 – 21 X

1.66 to 9.68 µg/m³

J&E 0.53 µg/m³


TCE: Sensitivity Analysis
Input parameters varied by 10%


cis-1,2-DCE: Predicted vs. Measured
2.1
0.6
0.05
2.14 to 2.67 μg/m³
1.5 – 45 X
0.06 to 1.46 μg/m³
J&E 0.04 μg/m³


trans-1,2-DCE: Pred. vs. Measured
0.09
0.03
0.01
0.09 to 0.13 μg/m³
1.3 – 7 X
0.02 to 0.07 μg/m³
J&E 0.002 μg/m³

Additional Case Studies

- Middlefield-Ellis-Whisman (MEW) site (CA)
- Lowry AFB (CO)

Middlefield-Ellis-Whisman (MEW) site

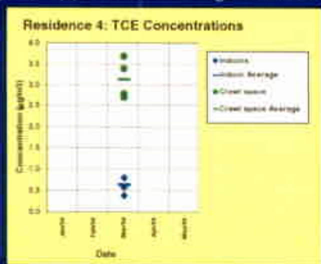
- South of Moffett field site

Middlefield-Ellis-Whisman (MEW) site

- One residence with crawl space
- TCE GW plume
- Approximately 5 ug/L under house with crawl space

Middlefield-Ellis-Whisman (MEW) site

- Data shows same pattern as before
  - Average is approx. 5 time higher in crawl space



Additional Case Studies

- Middlefield-Ellis-Whisman (MEW) site (CA)
- Lowry AFB (CO)
  - 5 residences with crawl space
  - Over chlorinated solvent plume
  - Sampled 6X in one year
  - TCE 1.6 – 6X higher in crawl spaces than indoors
  - Location since redeveloped

Crawl Spaces Conclusions I

- Crawl space concentrations higher than dwelling space concentrations in several case studies
- Using crawl space data as a surrogate for dwelling space measurements may result in the over prediction of risks
  - Potentially resulting in unnecessary cleanup

Crawl Space Conclusions II

- We have developed new models for buildings with crawl spaces and/or basements
- For the Moffett Field case study:
  - The standard Johnson and Ettinger Model (USEPA 2003) under-predicts both
    - Indoor vapor concentrations
    - Crawl space vapor concentrations

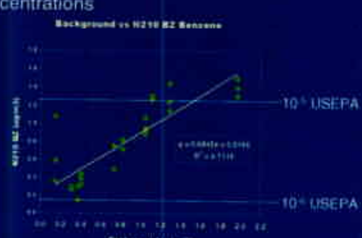
Ambient Air

- Johnson and Ettinger model assumes outdoor air has no contaminants

- Likely to be the case at most sites for chlorinated solvents
- BTEXs will be at levels above acceptable risks at all urban sites

Ambient Air Case Study

- Building 210 at Moffett Field (CA)
  - Over TCE plume but had high benzene concentrations



Ambient Air

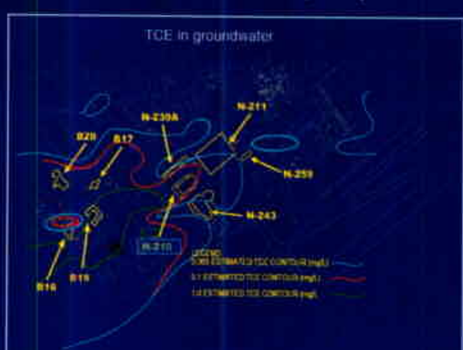
- Ambient air can represent a significant source of vapor intrusion
- Ambient concentrations can represent significant risks
- Our model account for intrusion of ambient air

Multi-Story Buildings

- J&E model assumes indoor air well mixed

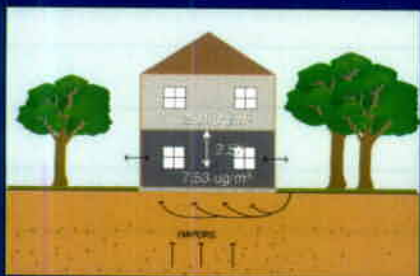
- Have already seen that this is incorrect for crawl spaces
- Now look at cement foundation buildings

Moffett Field (CA)



Building 210

- Two story slab-on-grade building



Multi-Story Buildings

- Both buildings with crawl spaces and cement foundations show concentration differences between floors
  - Not true for all buildings
- J&E model may then
  - Over predict concentrations above ground floor
  - Under predict concentrations on ground floor
- Partially incorporated into our model

Future Directions

- Current status - research model
- Step 1: Validate model with 10-15 case studies
- Step 2: Research more features/parameterization
  - Add soil gas sources, multiple soil layers
  - Incorporate multiple stories into model
  - Incorporate remedial options/costs
  - Examine existing default parameterization
    - Effect of ***overpressurization*** vs. underpressurization
    - Use LBL's COMIS & NIST's CONTAMW air flow models to better predict
      - Indoor/outdoor air exchange
      - Air exchange between floors
      - Pressure differentials
- Step 3: Develop public domain model

Appendix: Citations

- Turczynowicz, L. and Robinson, N. 2001. A model to derive soil criteria for benzene migrating from soil to dwelling interior in homes with crawl spaces. Human and Ecological Risk Assessment 7: 387-415.
- Waitz, M.F.W. et al. 1996. The VOLASOIL risk assessment model based on CSOIL for soils with volatile organic compounds.

Appendix: Sensitivity Analysis

- Following parameters were varied by ±10%:
  - Conc. in GW
  - Conc. in ambient air
  - Q_{soil}
  - Q_{crl}
  - Q_{bd}
  - θ_g (gas filled porosity)
  - θ_l (vapor filled porosity)
  - ρ (soil bulk density)
  - f_{oc}
  - k_{oc}
  - K_h (Henry's Law constant)
  - L_b (depth to gw below basement)
  - L_{cs} (depth to gw below cs)
  - $Volume_{cs}$
  - $Volume_{basement}$
  - $Volume_{dwelling}$

NATO OTAN Advanced Research Workshop

Risk Management Tools for Port Security, Critical Infrastructure, and Sustainability

NATO Advanced Research Workshop
16 – 19 March 2006, Venice, Italy
www.risk-trace.com/ports/index.php

Effective risk assessment and risk management at industrial ports and harbors requires consideration of numerous factors, including the protection and maintenance of critical infrastructure, emergency response planning, and the adoption of sustainable practices. Risk assessment and Risk management provide port and government authorities with the appropriate tools to prioritize security needs and to evaluate scenarios that can potentially impact the environment, cause injuries or fatalities, and result in both short- and long-term economic impacts. In order to be effective, these tools must continue to evolve from purely regulatory and scientific applications to techniques that capture and incorporate key stakeholder positions and viewpoints. It is often the case that available risk frameworks developed in the U.S. and elsewhere are applied to regional problems inappropriately and without adjustment for unique environmental, social, political, and economic conditions. Moreover, many of these frameworks are driven by country-specific regulatory regimes and political environments, and are not universally applicable to all situations and contexts. While risk assessors have an enormous array of methods and guidance documents from which to select, risk managers do not have an equivalent toolbox from which to obtain prescriptive decision-making advice on how best to address environmental security and sustainability concerns.

The goal of this ARW is to review the current practices and options for improvement of risk assessment and risk management practices to address the complex challenges of protecting, preventing, and responding to threats that jeopardize environmental security and critical infrastructure at industrial ports. The ARW will provide risk managers with a "tool box" of approaches and methods that are useful to promote the development and enhancement of programs for addressing environmental protection, security, and critical infrastructure. The value of incorporating a systematic understanding of stakeholder perspectives in projects that have fundamental environmental security and sustainability issues will be addressed. Various risk and decision analysis models will be reviewed through case studies; case studies will also be used to illustrate how retrospective and prospective evaluations of various security threats can be used to improve port operation practices, and to reduce the consequences of either natural or man-made disasters. This ARW will bring together security experts and scientists from NATO member and partner countries to share their experiences and expertise in environmental risk assessment, industrial port security programs, engineering, maritime shipping, and environmental regulation. This multidisciplinary perspective will provide ARW participants with a practical understanding of the current state-of-the art and the evolutionary changes that are required to develop effective risk management tools that appropriately consider environmental security and sustainability, and provide for risk-based and transparent decision-making.

Organizing Committee

I. Linkov, ARW Director, Cambridge Environmental Inc., USA
A. Ramadan, ARW Co-Director, National Center for Nuclear Safety, EGYPT
T. Bridges, U.S. Army Corps of Engineers, USA
S. Della Sala, Venice Port Authority, ITALY
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J. Valverde, Insurance Information Institute, USA
R. Wenning, ENVIRON International Corp., USA

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Linkov@CambridgeEnvironmental.com

SRA   Cambridge Environmental Inc   ENVIRON

Uncertainty in K_{ow} Values: Implications for Risk Assessment and Remedial Decisions for Contaminated Sites

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Cambridge Environmental Inc.

K_{ow} Definition and Application

- K_{ow} Definition:
  - Equilibrium ratio of the concentration of a chemical substance in n-octanol to that in water
- K_{ow} is widely used to:
  - Approximate the distribution of chemicals between aqueous and organic media
  - Estimate other physical properties and potential toxicity

Examples of K_{ow} Application

- Estimation of dermal permeabilities
- Estimation of absorption from the gastro-intestinal tract and lung
- Estimation of dissolved concentrations in water
- Estimation of bioconcentration coefficients between environmental media and living organisms
- Estimation of soil and sediment adsorption coefficients

Presentation Overview – Goals

- Evaluate the variation of K_{ow} for PCBs in EPA compiled or recommended databases
- Assess the potential cost implications of the use of a range of these values for site-specific remediation

Presentation Overview – K_{ow} Variation

- Causes of variation in reported K_{ow} values for PCBs:
  - Measurement Errors
  - Varying physical conditions (such as temperature)
  - Uncertainty due to mixture composition
  - Tabulation errors

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Presentation Overview – Cost Implications

- The selection of K_{ow} values can have significant cost implications for remediation.
- Example: Sediment Remediation at the Hylebos Waterways Superfund Site in Washington State
  - Establish Risk-based Sediment Quality Objectives (SQOs) using TrophicTrace software for different K_{ow} values tabulated by EPA
  - Calculate area required for remediation to meet specific remedial objectives
  - Calculate cost implications of selected K_{ow} values

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Presentation Overview – DoD Concerns

- Variation in K_{ow} values and other physicochemical properties affects remediation costs at DoD sites
- DoD should ensure values used for chemical properties in DoD risk assessments are correct
- DoD should be aware of inconsistencies in chemical properties reported in EPA databased and the implications for DoD sites

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Problems with Physicochemical Properties

- Literature values are not always reliable
- U.S. Chamber of Commerce has recently called on Congress to investigate why EPA refuses to stop disseminating faulty data used in the regulatory risk assessment process
- The Chamber is asking EPA to find a way to harmonize and improve the reliability of data
- To date, this has not happened

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Problems with K_{ow} Values

- In principle, K_{ow} is a well-defined and measurable property
- In practice, the K_{ow} values for many hydrophobic organic compounds are not well characterized
- Problems include:
  - Measurement Errors
    - Differing congener distributions, differing octanol/water ratios, differing temperatures
    - Experimental difficulties (e.g., presence of small quantities of emulsified octanol in the water phase)
  - Tabulation Errors
    - Inadequate documentation procedures
    - Incorrect citations

K_{ow} Measurement Variability – Small Sources

- Varying PCB congener distribution in an Aroclor
- Varying water/octanol volume ratio during measurement

K_{ow} Measurement Variability – Small Sources

- Consider a mass M of Aroclor 1254, containing mass $x_i M$ of congener i. The congeners are partitioned amongst a volume V_o of octanol and V_w of water. The two phases must contain the original mass, and each congener has its own partition coefficient K_i.

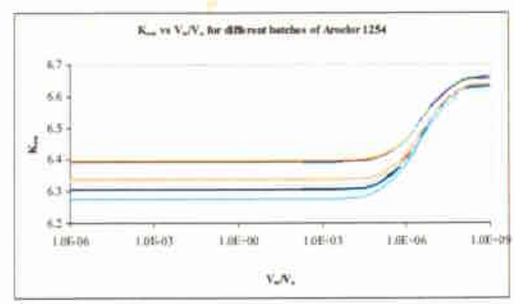
$$V_o C_{oi} + V_w C_{wi} = x_i M \qquad C_{oi} = K_i C_{wi}$$

where C_{oi} and C_{wi} are the concentrations of congener i in octanol and water, respectively. Solving for C_{oi} and C_{wi} and dividing their sums gives an overall K_{ow}:

$$\bar{K} = \frac{\sum_i C_{oi}}{\sum_i C_{wi}} = \frac{\sum_i \left(\frac{K_i x_i M}{V_o K_i + V_w}\right)}{\sum_i \left(\frac{x_i M}{V_o K_i + V_w}\right)} = \frac{\sum_i \left(\frac{K_i x_i}{K_i + \frac{V_w}{V_o}}\right)}{\sum_i \left(\frac{x_i}{K_i + \frac{V_w}{V_o}}\right)}$$

K_{ow} Measurement Variability – Small Sources

- Using known congener distribution data, we see that K_{ow} remains essentially constant until values of Vw/Vo exceeding 10^6, but even the whole range only imparts a variability of about 5%. This variation should never be of practical importance, as the EPA recommends a max water:octanol ratio of 50:1.



K_{ow} Measurement Variability – Small Sources

- Small sources of measurement variability
  - Varying temperature during measurement

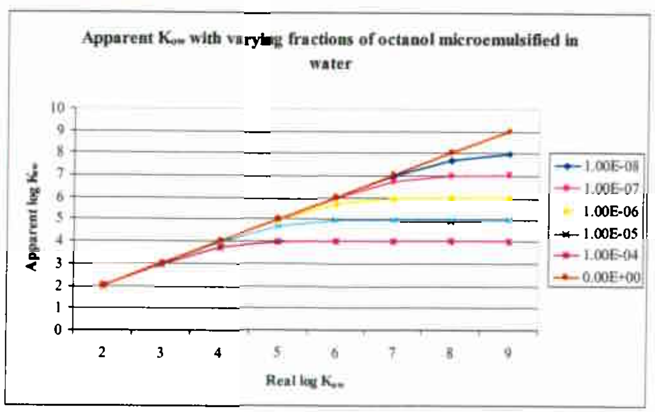
$$\ln K_{ow} = \ln K^0_{ow} + \left(\frac{\Delta H}{R}\right)\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

- For 21 PCB congeners for which data are available, a temperature difference of 25°C would, on average, make a difference of approximately 0.3 log units in the measurement

K_{ow} Measurement Variability – Large Sources

- Carefully carrying out the proper measurement procedure
  - When using shake-flask method to measure K_{ow} values, small amounts of octanol may become microemulsified in the water
  - Microemulsifications lead to errors in measurement which may be several log units for substances with high K_{ow}s
  - Using the slow-stir method is a safer option

K_{ow} Measurement Variability – Large Sources



K_{ow} Tabulation Errors

- EPA frequently references databases outside its web space without proper discussion of their drawbacks
  - PhysProp
  - ChemFate
    - Partially funded by EPA
    - Problem: log K_{ow} value of 3.90 for total PCBs
    - Incomplete examination and misinterpretation of references

K_{ow} Tabulation Errors

- EPA also references Mackay *et al.*'s (1992) *Illustrated Handbook of Physical-Chemical Properties*
  - Also tangled web of references
  - Shows citations to irrelevant papers rather than misinterpreted papers

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ChemFate: Total PCBs

ChemFate
(3.90 recommended, 3.9-6.7 range given)

Weber (1983)
3.9 6.7

Tulp and Hutzinger (1978)
(identifies 3.9 as erroneous value)

Metcalf et al. (1975)
(3.9 calculated)

Chiou et al. (1977)
(Paper uses shake-flask method to derive equation relating coefficient with aqueous solubility; does not itself mention total PCBs)

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Mackay: Aroclor 1254

Mackay (1992)

6.03

Hansch et al. (1973)

Callahan et al. (1979)

Mabey et al. (1982)

Chiou et al. (1977)

Hansch et al. (1974)

6.47

Veith & Kosian (1983)

Zaroogian (1985)

Veith et al. (1979)

Measured using reverse-phase high-pressure liquid chromatography; methodology described in Veith & Morris (1978)

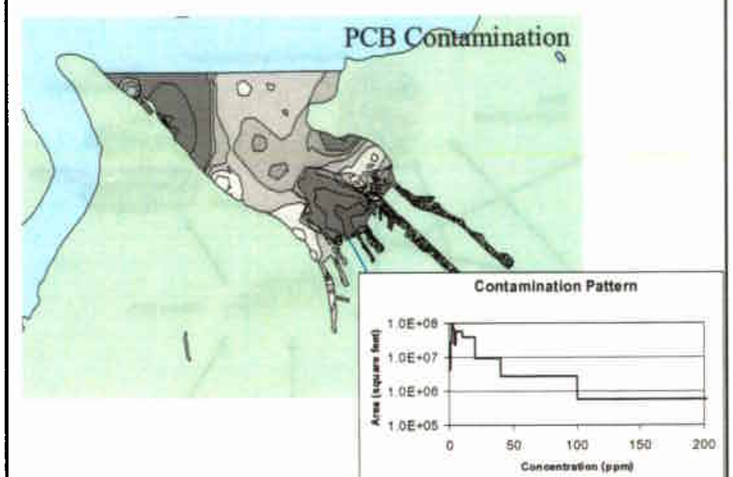
Paper uses shake-flask method to measure different partition coefficients, including those of three PCB congeners; derives equation relating coefficient with aqueous solubility; does not, however, mention Aroclor 1254 or report a partition coefficient value of 6.03 for any substance

Paper actually published in 1975; paper does not mention Aroclor 1254 or report a value of 6.03; paper describes a structure-activity relationship for anesthetic gases which is irrelevant to PCBs

Reason for direct citation by Mackay is unclear; paper does not mention Aroclor 1254 or report a value of 6.03; paper describes a structure-activity relationship for chloramphenicols which is irrelevant to PCBs

19

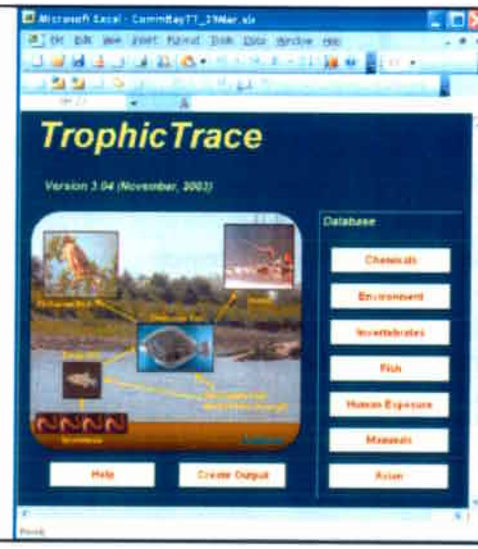
Case Study: Hylebos Waterways Superfund Site



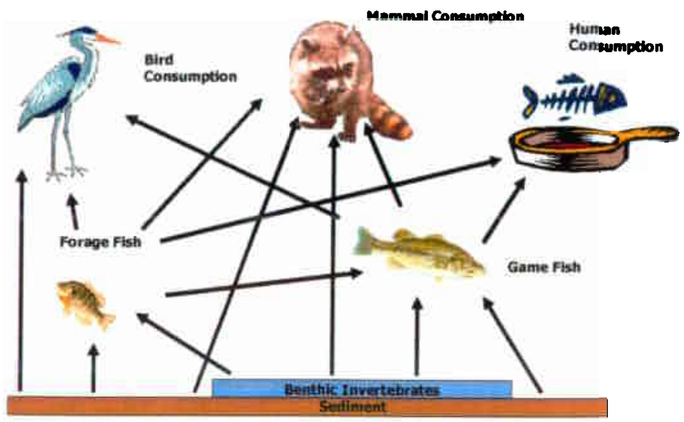
Case Study: Superfund Site History

- Human health and ecological risk assessment
- 1989 ROD established Sediment Quality Objectives
  - A site-specific biota-to-sediment accumulation factor (BSAF) was calculated based on available fish tissue and sediment data.
  - SQO for PCBs was set at 150 ppb
- 1997 EPA revision
  - Input parameters and fish consumption rates were changed
  - SQO for PCBs was set at 300 ppb
- Alternative Approach to SQO: use of bioaccumulation modeling

21



Case Study: Conceptual Model



Case Study: Gobas Bioaccumulation Model

$$C_f = \frac{k_1 \times C_{wd} + k_d \times C_{diet}}{k_2 + k_e + k_m + k_g}$$

C_f concentration of PCBs in fish tissue (μg/kg);
C_{wd} freely dissolved concentration of PCBs in water (μg/L);
C_{diet} concentration of PCBs in the diet (μg/kg);
k_1 gill uptake rate (L/kg-d);
k_d dietary uptake rate (1/d);
k_2 gill elimination rate (1/d);
k_e fecal elimination rate (1/d);
k_m metabolic rate (1/d); and
k_g growth rate (1/d).

K_{ow} enters the model both through C_{wd} and C_{diet} and through the calculation of PCB uptake, elimination, and metabolic rates

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Case Study: SQOs and Cost Calculation

$$HQ = \frac{IR_f \times C_f \times ED}{BW \times RfD \times AT \times 10^6}$$

Risk-based cleanup levels were back-calculated using TrophicTrace based on an HQ value of 1.

$$Cost = (AreaCont > SQO) * (DrDepth) * (DrUnitCost)$$

TrophicTrace Calculation

Assumed

Based on EPA estimates

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Case Study: Total PCBs & Aroclor 1254

Database	Log K_{ow} Total PCBs	Log K_{ow} Aroclor 1254
KowWin (calculated)	6.34	6.98
KowWin (experimental)	6.29	6.79
PhysProp	7.10	6.50
ChemFate	3.9	
Water9	7.31	6.03
Chem9	7.31	3.34
SCDM	6.70	
SCDMWin	6.04	
Superfund PHEM	6.04	
STF	8.23	6.04
HHRAP		6.21
PBT Profiler	6.3	6.8
ATSDR		6.50

Log Kow values were downloaded in early 2004.

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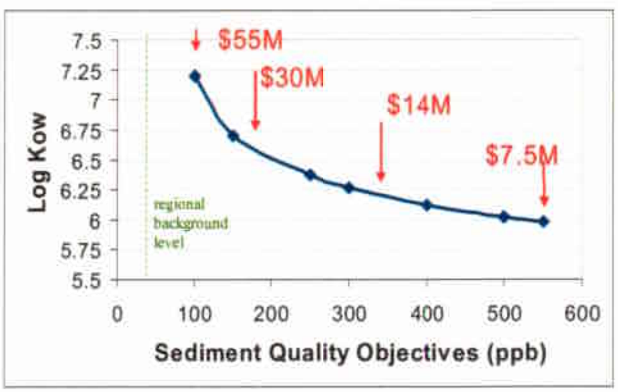
Case Study: SQOs & Costs vs. K_{ow}



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K_{ow} Problems

- PCBs are not the only chemicals with poor K_{ow} literature
  - Pontolillo and Eganhouse (2001) found similar problems in an earlier investigation of the DDT and DDE literature
  - Another example of differing log K_{ow}s:

Chemical	ChemFate	PhysProp	ATSDR	Other
Di-N-Octyl Phthalate	**5.22**	**8.10**	**5.22**	**9.2***

* http://www.epa.gov/waterscience/itm/total.pdf (EPA Inland Testing Manual, 1998)

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Adjusting Inconsistent Chemical Properties

- Physicochemical properties used in fate and transport modeling in risk assessments should be internally consistent
- For example, Kow values should be consistent with octanol-air and air-water partition coefficients
- Schenker et al. have developed a method for harmonizing inconsistent physicochemical properties using a least-squares adjustment procedure

(Schenker, U., MacLeod, M., Scheringer, M., and Hungerbuhler, K. (2005). Environ. Sci. Technol., 39(21) pp. 8434-8441.)

29

Adjusting Inconsistent Chemical Properties

- Least-squares adjustment procedure minimizes the adjustment of literature derived values
- Also allows the propagation of uncertainties from the literature to the final derived values

30

Conclusions

- Variation of the K_{ow} value can have a large and usually unexamined cost implication for site remediation.
- Lack of data quality procedures and the proliferation of erroneous data and references may be responsible for the wide range of K_{ow}.
- Rigorous data quality and peer review procedures are required to ensure a consistent use of meaningful K_{ow} values.

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Approaches to Prioritization of Materials of Evolving Regulatory Interest (MERIT)

Igor Linkov[1], Kyle Satterstrom[1], Todd S. Bridges[2], Jongbum Kim[2], Burton Suedel[2], Jeff Steevens[2], and Shanna Collie[3]

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24 January 2006

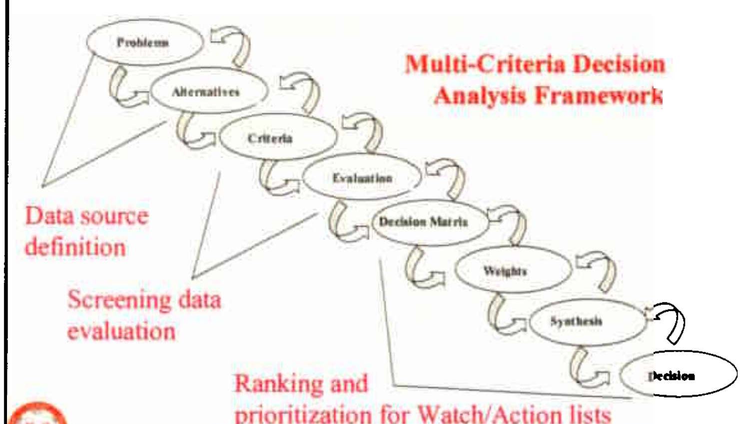
Overview

- MERIT's challenges
- Introduction to Multi-Criteria Decision Analysis (MCDA)
- Examples of MCDA uses in cases relevant to MERIT
  - Use of MCDA for Risk Assessment
  - Use of MCDA and Risk Assessment for remedial alternative selection
  - Use of MCDA for strategic planning and prioritization
- Conclusion
- References

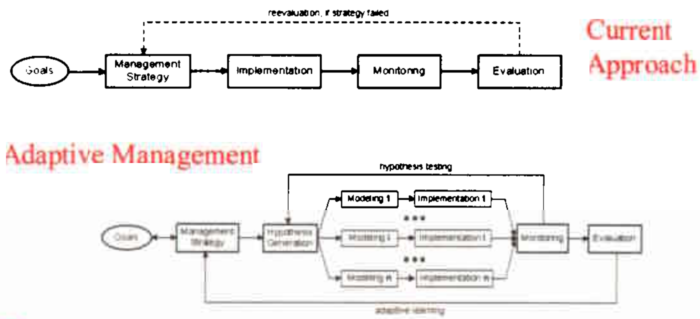
MERIT's Challenges

- Be proactive as opposed to reactive in risk management
- Effectively allocate and leverage resources across DOD Service Branches
- Use up-to-date data and analytical techniques
- Effectively evaluate substitute chemicals

How Can RA, MCDA, and AM Help MERIT?

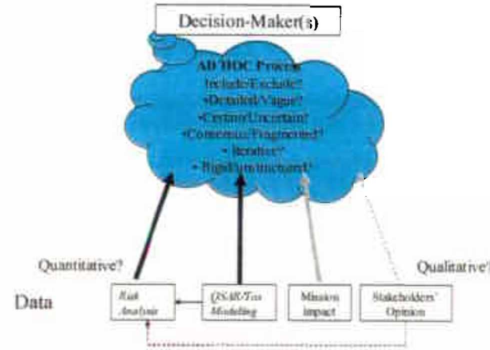


From Compliance to Sustainable Management



after Linkov et al., 2006

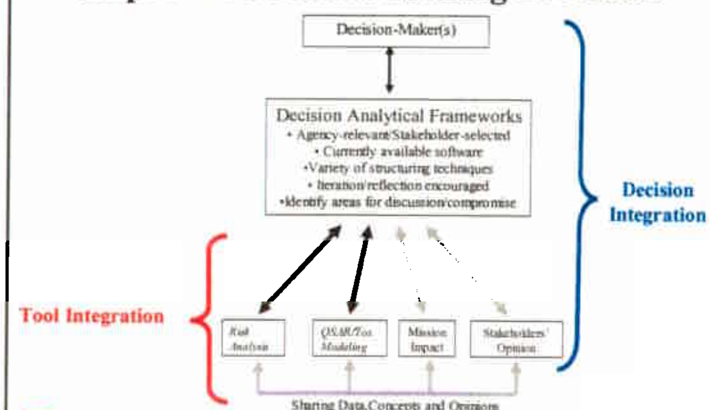
Unstructured Decision-Making



Challenges Posed by Complex Decision-Making

- "Humans are quite bad at making complex, unaided decisions" (Slovic *et al.*, 1977)
- Individuals respond to complex challenges by using intuition and/or personal experience to find the easiest solution
- At best, groups can do about as well as a well-informed individual
- Groups can devolve into entrenched positions resistant to compromise
- "There is a temptation to think that honesty and common sense will suffice" (IWR-Drought Study p.vi)

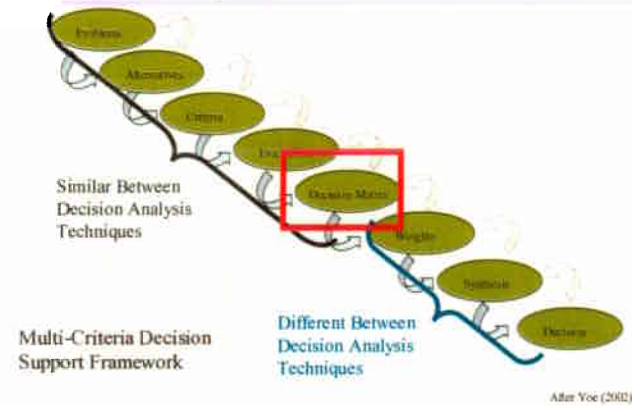
Improved Decision-Making Processes



Benefits of Multi-criteria decision analysis (MCDA)

- MCDA methods provide a means of integrating various inputs with stakeholder values
- MCDA methods provide a means of communicating modeling/monitoring outputs for scenario planning and stakeholder understanding
- **Risk-based MCDA** offers an approach for organizing and integrating varied types of information to perform rankings and to better inform decisions

Decision Analysis and Decision Tools



Simple Decision Matrix

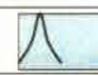
Criteria / Materials	Public health *[Cancer Risk]*	Environmental Impact *[Residue mg/L]*	Weapon Effectiveness *[Ranking]*
Chemical A	2.8 E -5	10	1
Chemical B	2.8 E -5	2	2
Chemical C	2.8 E -5	2	3-4
Chemical D	2.0 E -5	4	3-4

Possible evaluation without MCDA tools

Realistic Decision Matrix

How to combine these criteria?

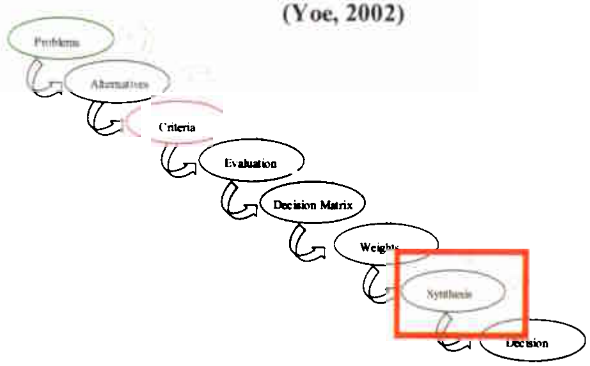
How to compare these alternatives?

	Criteria 1	Criteria 2	Criteria 3	Criteria 4
Alt. 1	How to interpret these results?			
Alt. 2	Monitoring Results	Stakeholder Preference	Economic Cost	Non-monetary benefit
Alt. 3		Stakeholder Preference	Economic Cost	Non-monetary benefit
Alt. 4		Stakeholder Preference	 ost	Non-monetary benefit

MCDA tools may be required for decision making

Multi-Criteria Decision Analysis

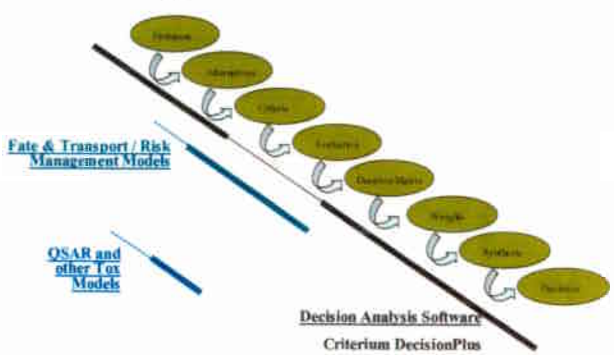
(Yoe, 2002)



Multi-Criteria Decision Analysis

- Multi-Criteria Decision Analysis (MCDA) methods
  - Evolved as a response to the observed inability of people to effectively analyze multiple streams of dissimilar information
  - Many different MCDA approaches
- Based on different theoretical foundations (or combinations)
  - Optimization models
  - Goal aspiration
  - Outranking models

Linking Tools for MERIT



Case Studies

- Risk-based MCDA provides:
  - Organized, analytical process to assess emerging contaminants
  - Facilitates quantitative evaluation and decision-making
  - Approach to evaluate competing management actions
  - Means to prioritize scarce management resources
- Illustration through 3 case studies relevant to MERIT Program:
  - Use of MCDA for Risk Assessment
  - Use of MCDA and Risk Assessment for remedial alternative selection
  - Use of MCDA for strategic planning and prioritization

Case 1: Use of MCDA in Ecological Risk Assessment

- Setting: A contaminated lake; affected ecological receptors
- Remedial Alternatives:
  - No action
  - Comprehensive dredging
  - Hot spot dredging
- **Multiple receptors and lines of evidence for ecological impact**

Eco Risk Assessment: Assessment Endpoints

- Invertebrates
  - Freshwater mussels
- Fish
  - Largemouth Bass
  - Bluegill
  - American Eel
- Birds
  - Great blue heron
  - Belted kingfisher
  - Osprey
- Mammals
  - Raccoon
  - Mink

Case 1

Measurement Endpoints

- Survival, Growth, and Reproduction of Benthic Invertebrate Community
  - Comparison surface water and sediment COCs to benchmarks
  - Sediment toxicity tests
  - Benthic community bioassessment
  - Invertebrate tissue analysis – comparison to species-specific TRVs (Toxicity Reference Values)
- Health of Fish Community
  - Measurement of COCs in surface water and sediment
  - Survey and observation of fish
  - Fish tissue analysis – comparison to species-specific TRVs

Case 1

Measurement Endpoints (cont.)

- Health of Piscivorous Bird Community
  - Survey and observation of aquatic birds
  - Trophic food-chain modeling of dietary intake of COCs and comparison to species-specific TRVs
- Health of Piscivorous Mammal Community
  - Survey and observation of aquatic mammals
  - Trophic food-chain modeling of dietary intake of COCs and comparison to species-specific TRVs

Case 1

Expert Choice

Software Demonstration

Case 1

MCDA Use for Risk Assessment: Relevance to MERIT Program

- MERIT needs:
  - Chemical Assignment to Watch List
  - Chemical Assignment to Action List
  - Migration from Watch to Action List
- Problems:
  - Properties of chemicals unknown
  - Multiple ways to assess toxicity and risk (QSAR, expert judgment, limited empirical data, modeling, etc.)
  - Multiple criteria to incorporate into decision
- Solution: integration of technical information using MCDA

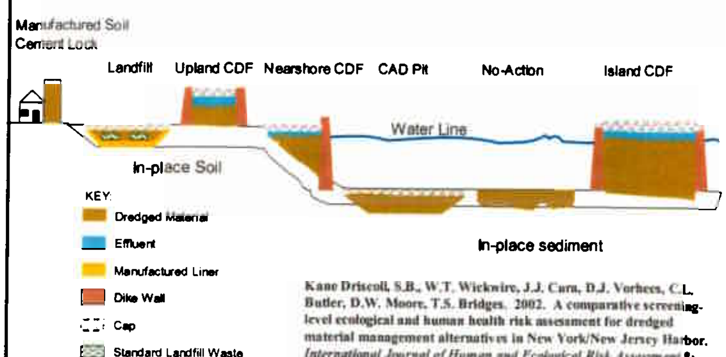
Case 1

Case 2: Use of MCDA and Risk Assessment for Selection of Remedial Alternative for New York Harbor

- Environmental remediation and restoration for contaminated sediments
- Multiple alternatives available
- Each alternative has associated costs and risks
- Multiple stakeholders with varying objectives and values

Case 2

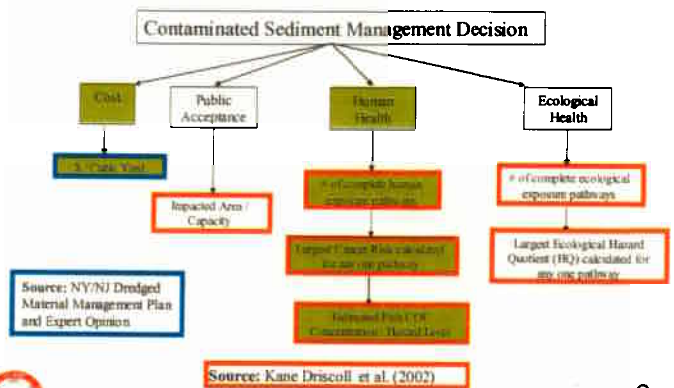
NY Sediment Management Alternatives



Kane Driscoll, S.B., W.T. Wickwire, J.J. Cura, D.J. Vorhees, C.L. Butler, D.W. Moore, T.S. Bridges. 2002. A comparative screening-level ecological and human health risk assessment for dredged material management alternatives in New York/New Jersey Harbor. *International Journal of Human and Ecological Risk Assessment* 8: 603-626.

Case 2

Decision Criteria: NY/NJ Harbor



Case 2

Criteria Levels for Each Alternative

Alternatives	Cost ($/CY)	Public Acceptability: Impacted Area/Capacity (acres / MCY)	Ecological Risk: Ecological Exposure Pathways	Ecological Risk: Magnitude of Ecological HQ	Human Health Risk: Human Exposure Pathways	Human Health Risk: Magnitude of Maximum Cancer Risk	Human Health Risk: Estimated Fish COC / Risk Level
CAD	5-29	4400	23	680	18	2.8 E-5	28
Island CDF	25-35	980	38	2100	24	9.2 E-5	92
Near-shore CDF	15-25	6500	38	900	24	3.8 E-5	38
Upland CDF	20-25	6500	38	900	24	3.8 E-5	38
Landfill	29-70	0	0	0	21	3.2 E-4	0
No Action	[illegible]	0		[illegible]	12	2.2 E-4	220
Cement-Lock	54-75	0	14	0.00002	25	2.9 E-5	0
Manufactured Soil	54-60	750	18	8.7	22	1.8 E-3	0

Blue Text: Most Acceptable Value

Red Text: Least Acceptable Value

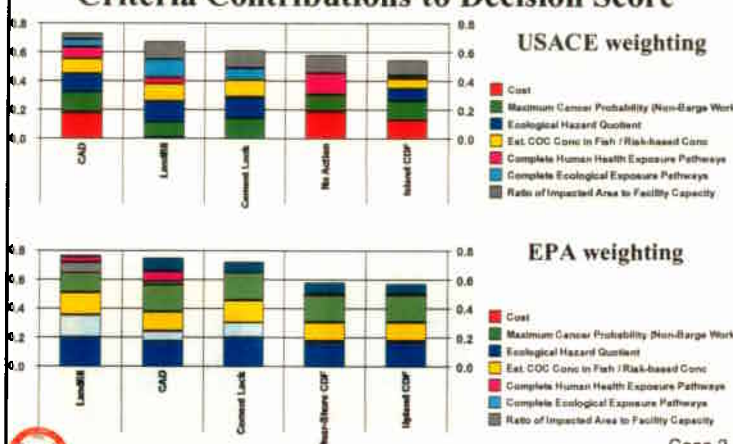
Case 2

USACE/EPA Survey Results: Criteria Weights (%)

	Cost	Public Acceptability	Human Health Risk	Ecological Risk
EPA	10	7.4	47	35.6
Army Corps	19.7	12.5	40.7	27.1

Case 2

Criteria Contributions to Decision Score



Case 2

MCDA and RA use for Remedial Alternative Selection: Relevance to MERIT Program

- MERIT needs:
  - Integration of Risks and Decision
  - Ranking of Alternative Courses of Action
  - Multiple Stakeholders
- Problems:
  - Uncertainty in Risks
  - Multiple Stakeholders with Unique/Specific Priorities
  - Multiple Criteria
- Solution: Use of integrated MCDA and RA approach

Case 2

Prioritization

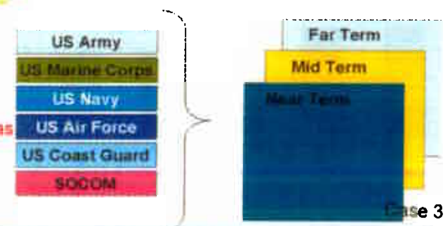
- Limited resources are available for research on any MERIT compound
  - Thus, must prioritize compounds for further assessment and guidance development
  - Different materials pose risks of varying kinds and degrees
    - The values placed on these materials and associated risks will differ for DoD and stakeholders
  - New technologies and science evolve rapidly, posing additional challenges to prioritization efforts and decision making

Case 3: Small Arms Technology Gap Prioritization

Required as a Part of **Joint** Capabilities Integration and Development System

Methodology is not developed

Service Branches have own ideas and priorities



Case 3

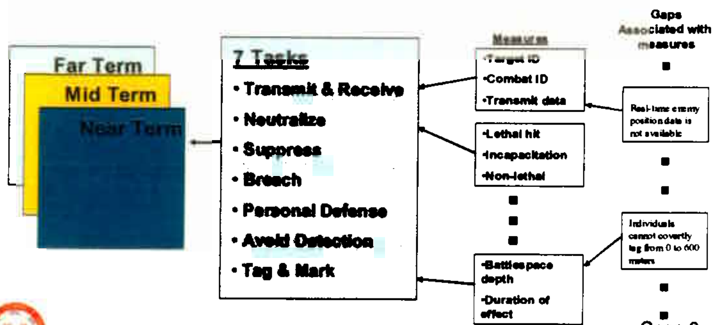
Approaches to Prioritization

- Available Approaches for Prioritization:
  - Subjective Prioritization (Gut Feeling)
    - Pros: easy to do
    - Cons: no rigor, potential mistakes, not transparent and not reliable
  - Ad hoc weighting using Excel Spreadsheets
    - Pros: everybody can use Excel, relative ease of implementing
    - Cons: requires arbitrary weighting for multiple criteria, difficult to modify/adjust for specific service branches
  - Multi-Criteria Decision Analysis
    - Pros: transparent, state-of-the-art tool, can be tailored/modified in real time, records and visualizes differences among service branches' or individuals' opinions
    - Cons: relatively intense, may require advanced sensitivity analysis

Case 3

Selected Approach

Decision hierarchy, tasks, and measures were taken directly from military doctrine; personnel were surveyed to assess relative weights by service branch



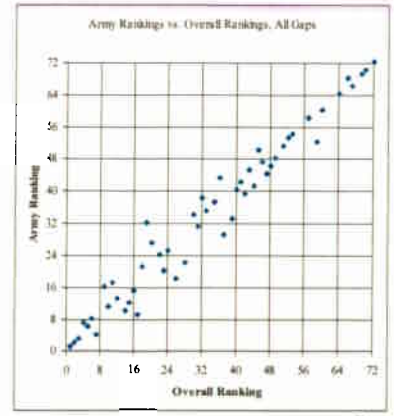
Case 3

1. List of 72 technology gaps prioritized for each service branch

2. Overall ranking and identification of priority gaps

3. Assessment of uncertainty and variability of ranking within each service branch and across multiple branches

Individual commands rankings were quite similar to the consensus ranking results



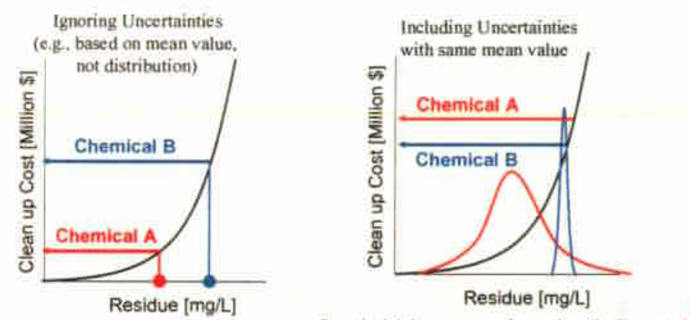
Case 3

MCDA Use for Strategic Planning & Prioritization: Relevance to MERIT

- Needs:
  - Strategic priorities and planning
  - Budget allocation
  - Prioritization of chemicals in the Watch and Action Lists
  - Coordination with OMB
- Problems:
  - Need to integrate technical and social factors
  - Multiple stakeholders with often diverging priorities
  - Uncertainty
- Solution: Use of MCDA

Case 3

Why the uncertainties matter



• For simplicity, assume the clean up costs for a unit conc. of two chemicals are same

Chemical A has more variance than B. Expected cost [EC] = Sum of probability of each residue of a chemical multiplied by its cost

Chemical A's EC >> Chemical B's EC

Decision Changes!!!!

DOD Directive 4715.1 and MCDA, RA and AM Tools

DOD Directive 4715.1	MCDA	AM	Risk Assessment
4.1 Manage & apply DoD installation assets to sustain DoD mission	+	+	
4.2 Use Defense Installations Strategic Plan to guide ESOH decision-making	+	+	+
4.3 Use ESOH management systems in military planning	+		
4.4 Ensure all organizations plan, program, & budget to manage ESOH risks	+		
4.5 Optimum resource allocation	+	+	
4.6 Ensure tenants comply with laws and DoD policies.			+
4.7 Protect DoD personnel from accidental death, injury or occupational illness.			+
4.8 Protect the public from risks because of DoD activities			+
4.9 Establish and maintain open and productive ESOH dialogue	+		

Conclusion

- Risk-based MCDA provides:
  - Organized, analytical process to assess emerging contaminants
  - Facilitates quantitative evaluation and decision-making
  - Approach to evaluate competing management actions
  - Means to prioritize scarce management resources

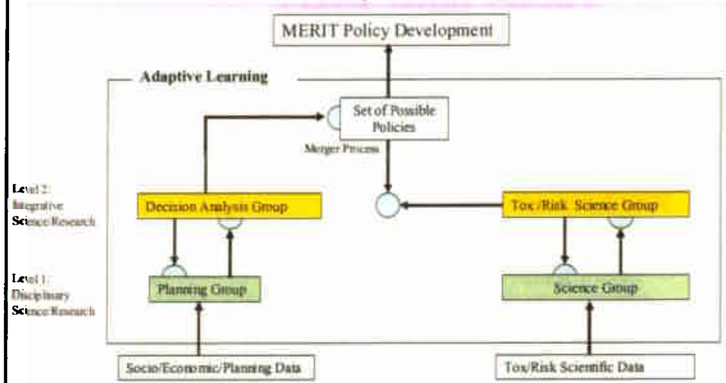
References

- Decision Analysis with USACE Examples
  - Trade-Off Analysis
    - http://www.iwr.usace.army.mil/iwr/pdf/tradeoff.pdf
  - Beyond Expected Value
    - http://www.iwr.usace.army.mil/iwr/pdf/02r4bey_exp_val.pdf
  - MCDA Workshop Sites with Posted Lectures
    - http://www.risktrace.com/sediments
    - http://www.risktrace.com/nato
- Papers

- Linkov, I., Varghese, A., Jamil, S., Seager, T.P., Kiker, G., Bridges, T. (2004). "Multi-Criteria Decision Analysis: Framework for Applications in Remedial Planning For Contaminated Sites". In Linkov, I. And Ramadan, A. eds "Comparative Risk Assessment and Environmental Decision Making" Kluwer, 2004.
- Kiker, G., Bridges, T., Varghese, A.S., Seager, T.P., and Linkov, I. (2005). Application of multi-criteria decision analysis in environmental management. *Integrated Environmental Assessment and Management* 1 v. 2 49-58.
- Linkov, I., Satterstrom, K., Kiker, G., Bridges, T., Benjamin, S., Belluck, D. (2006). From Optimization to Adaptation: Shifting Paradigms in Environmental Management and Their Application to Remedial Decisions. *Integrated Environmental Assessment and Management* 2 v1 92-98.
- Linkov, I., Satterstrom, K., Seager, T.P., Kiker, G., Bridges, T., D. Belluck, A. Meyer (2006). "Multi-Criteria Decision Analysis: Comprehensive Decision Analysis Tool for Risk Management of Contaminated Sediments". *Risk Analysis* 26 v.1 1-18
- Linkov, I., Satterstrom, K., Kiker, Batchelor, C., G., Bridges, T.(2006, in press). From Comparative Risk Assessment to Multi-Criteria Decision Analysis and Adaptive Management: Recent Developments and Applications. *Environment International.*

Additional Slides

MERIT Policy Development



After C. F. Kiker *et al.* / *Ecological Economics* 37 (2001) 403 - 416
Based on Adaptive Resonance Theory - Grossberg (1982)

Risk-Based Multi-Criteria Decision Analysis

- Definition: set of tools & techniques to:
  - Describe objectives, alternatives, uncertainties
  - Provide framework, guidance for complex decisions
  - Good Outcome vs. Good Decision
    - e.g., winning a lottery by luck is a good outcome but choosing to invest in lottery tickets may not be good decision
- To bridge the gap in decision-making between science uncertainties and values of stakeholders and decision makers

Risk-Based Multi-Criteria Decision Analysis (Cont.)

- Displaying tradeoffs among objectives
  - Relative advantages and disadvantages of using a material
- Helping stakeholders reflect upon, articulate, and apply value judgments
  - Resulting in a ranking of alternatives
- Explicitly consider the risks (uncertainties) associated with emerging contaminants

Multi-Criteria Decision Analysis and Tools

- See Yoe 2002 (Web address in Reference Section)
- Simplified methods
  - "Pros and cons"
  - Maximin and Maximax
  - Decision tree
  - Influence diagrams
- Multi-attribute utility/value theory (MAUT)
- Analytical Hierarchy Process (AHP)
- Outranking

Analytical Hierarchy Process (after Dyer)

- Determines the weights on objectives, and the performance of alternatives on these objectives by pair-wise comparison.
- Assumes that the weights of objectives are independent of the scale used for the evaluation of alternatives.
- Steps Followed:
  - Decide the overall objective (goal) of the decision
  - Develop a hierarchy of objectives
  - Identify a unique, measurable attribute for every sub-objective
  - Identify the alternatives available
  - Assess performance of alternatives on every objective on a scale of 1-9 (by pair-wise comparison for all combinations of alternatives)
  - Assign weights to objectives (by pair-wise comparison of all objectives.)

Multi-Attribute Utility Theory (after Dyer)

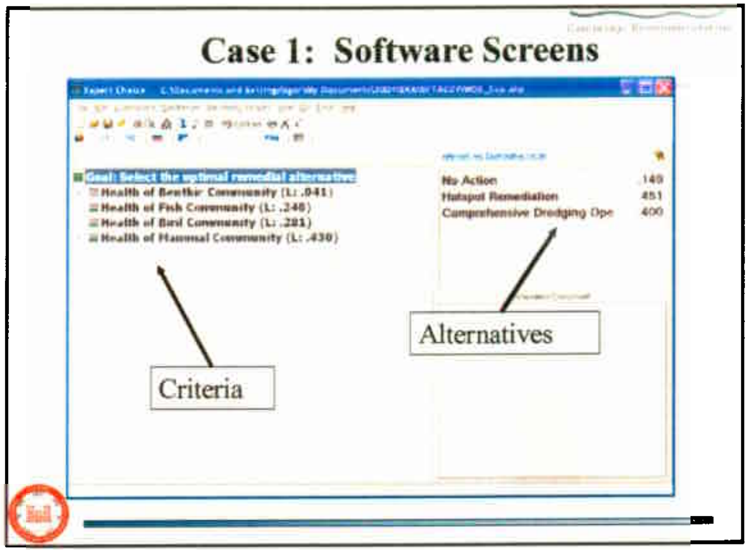
- Seeks the performance of alternatives on objectives explicitly in terms of utility functions. The assessment of utility functions incorporates the information about the range over which the alternatives vary.
- Weights of objectives can be specified directly or by pair wise comparison.
- Steps Followed:
  - Decide the overall objective (goal) of the decision
  - Develop a hierarchy of objectives
  - Identify unique, measurable attribute (measure) for every sub-objective. Specify the utility curves for each of these measures.
  - Identify the alternatives available
  - Estimate the performance of every alternative on every measure.
  - Assign weights to objectives by direct assessment or tradeoff analysis.

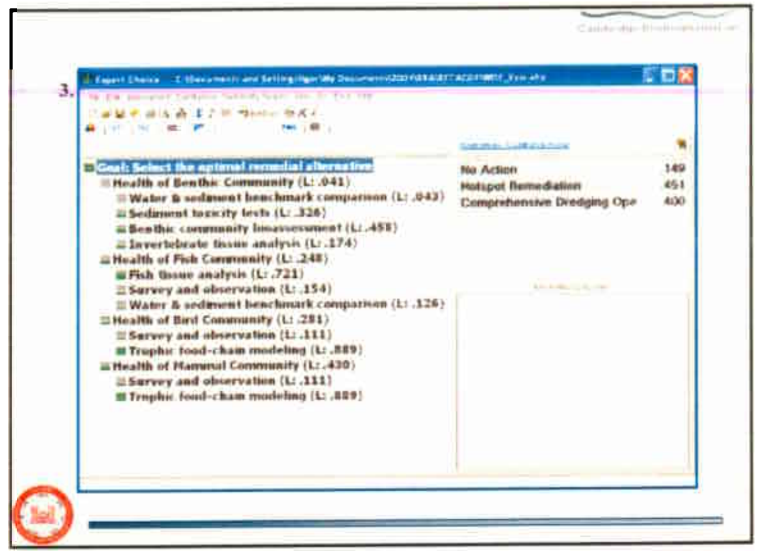
Decision Analysis Methods and Tools

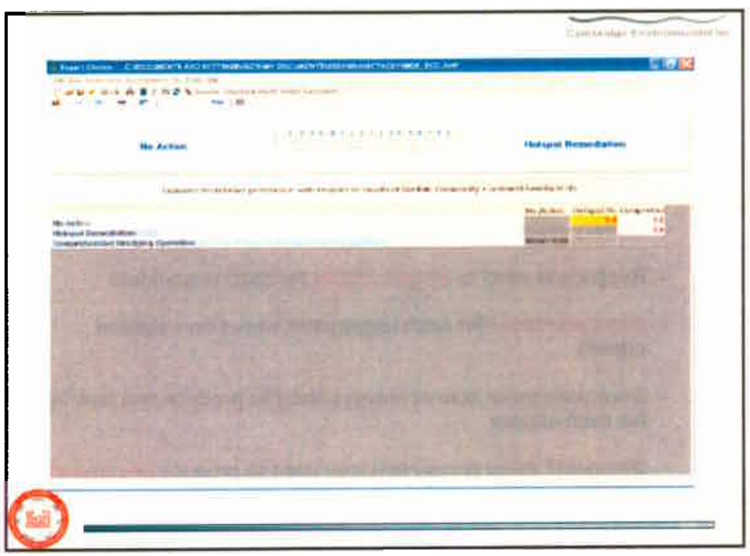
Elements of Decision Process	*Ad Hoc* Decision Making	Comparative Risk Assessment	Multi-Criteria Decision Analysis
Define problems	Stakeholder input limited or non-existent. Therefore, stakeholder concerns may not be addressed by alternatives.	Stakeholder input collected after the problem is defined by decision-makers and experts. Problem definition is possibly refined based on stakeholder input.	Stakholder input incorporated at beginning of problem formulation stage. Often provides higher stakeholder agreement on problem definition. Thus, proposed solutions have a better chance at satisfying all stakeholders.
Generate alternatives	Alternatives are chosen by decision-maker usually from pre-existing choices with some expert input.	Alternatives are generated through formal involvement of experts in more site-specific manner.	Alternatives are generated through involvement of all stakeholders including experts. Involvement of all stakeholders increases likelihood of novel alternative generation.
Formulate criteria by which to judge alternatives	Criteria by which to judge alternatives are often not explicitly considered and defined.	Criteria and subcriteria are often defined.	Criteria and subcriteria hierarchies are developed based on expert and stakeholder judgment.
Gather value judgments on relative importance of criteria	Non-quantitative criteria valuation weighted by decision maker	Quantitative criteria weights are sometimes formulated by the decision maker, but in a poorly justified manner.	Quantitative criteria weights are obtained from decision makers and stakeholders.
Rank/select final alternatives	Alternative often chosen based on implicit weights in an opaque manner.	Alternative chosen by aggregation of criteria scores through weight of evidence discussions or qualitative considerations.	Alternative chosen by systematic, well-defined algorithms using criteria scores and weights.

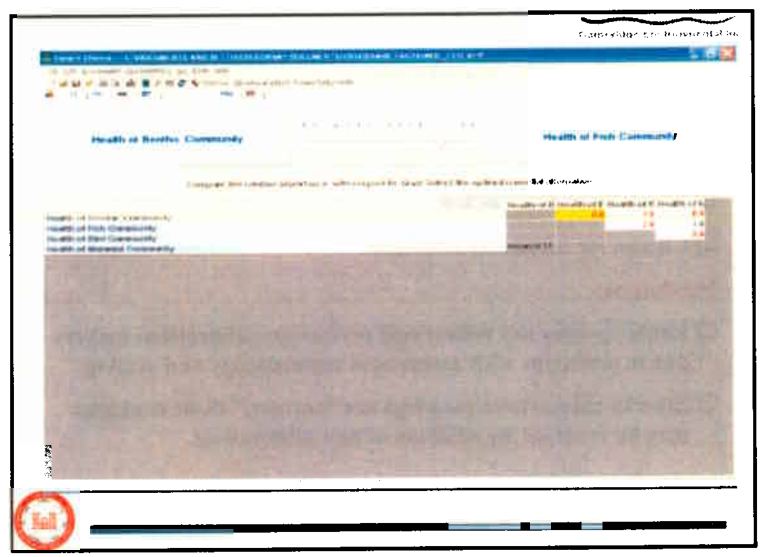
Decision Analysis Methods and Tools: Comparison

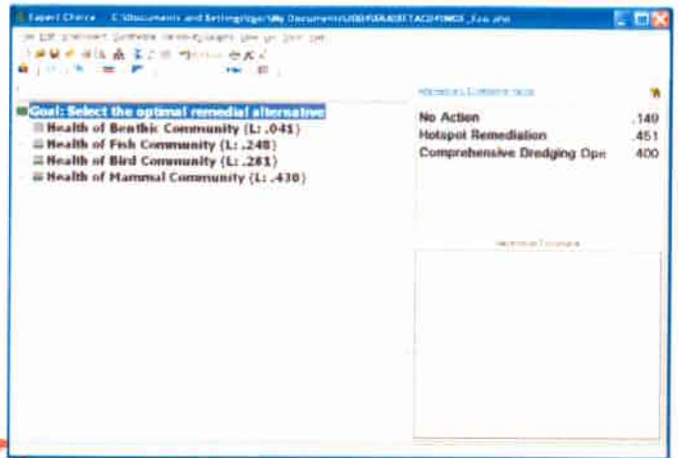
Method	Important elements	Strengths	Weaknesses
Multi-attribute utility theory	Expression of overall performance of an alternative in a single, non-monetary number representing the utility of that alternative. Criteria weights often obtained by directly surveying stakeholders	Easier to compare alternatives whose overall scores are expressed as single numbers. Choice of an alternative can be transparent if highest scoring alternative is chosen. Theoretically sound — based on utilitarian philosophy. Many people prefer to express net utility in non-monetary terms	Maximization of utility may not be important to decision makers. Criteria weights obtained through less rigorous stakeholder surveys may not accurately reflect stakeholders' true preferences. Rigorous stakeholder preference elicitations are expensive
Analytical hierarchy process	Criteria weights and scores are based on pairwise comparisons of criteria and alternatives, respectively	Surveying pairwise comparisons is easy to implement	The weights obtained from pairwise comparison are strongly criticized for not reflecting people's true preferences. Mathematical procedures can yield illogical results. For example, rankings developed through AHP are sometimes not transitive
Outranking	One option outranks another if: 1) "it outperforms the other on enough criteria of sufficient importance (as reflected by the sum of criteria weights)" and 2) it "is not outperformed by the other in the sense of recording a significantly inferior performance on any one criterion". Allows options to be classified as "incomparable"	Does not require the reduction of all criteria to a single unit. Explicit consideration of possibility that very poor performance on a single criterion may eliminate an alternative from consideration, even if that criterion's performance is compensated for by very good performance on other criteria	Does not always take into account whether over-performance on one criterion can make up for under-performance on another. The algorithms used in outranking are often relatively complex and not well understood by decision makers


Case 1: Software Screens
Goal: Select the optimal remedial alternative
Health of Benthic Community (L: .041)
Health of Fish Community (L: .248)
Health of Bird Community (L: .281)
Health of Mammal Community (L: .430)
No Action 149
Hotspot Remediation 451
Comprehensive Dredging Ope 400
Criteria
Alternatives

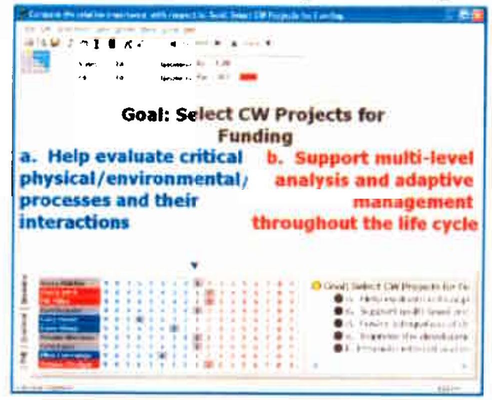

3.
Goal: Select the optimal remedial alternative
Health of Benthic Community (L: .041)
Water & sediment benchmark comparison (L: .043)
Sediment toxicity tests (L: .326)
Benthic community bioassessment (L: .458)
Invertebrate tissue analysis (L: .174)
Health of Fish Community (L: .248)
Fish tissue analysis (L: .721)
Survey and observation (L: .154)
Water & sediment benchmark comparison (L: .126)
Health of Bird Community (L: .281)
Survey and observation (L: .111)
Trophic food-chain modeling (L: .889)
Health of Mammal Community (L: .430)
Survey and observation (L: .111)
Trophic food-chain modeling (L: .889)
No Action 149
Hotspot Remediation 451
Comprehensive Dredging Ope 400


No Action
Hotspot Remediation


Health of Benthic Community
Health of Fish Community



ExpertChoice Software: Systematic Decisions from Groups of People



Strengths and Weaknesses of AHP Analysis

Strengths

- ❑ Easy to use: Pair-comparisons can be done easily
- ❑ Pre-defined Scale of 1-9
- ❑ Checks for inconsistencies also

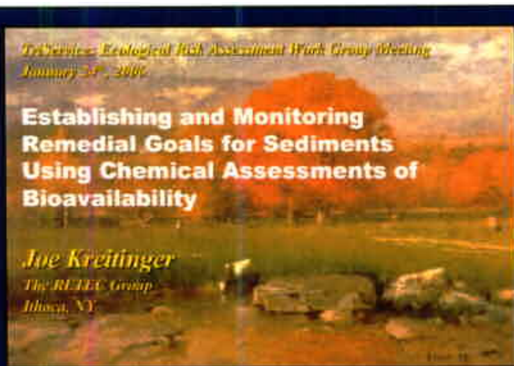
Weaknesses

- ❑ Rankings may not reflect real preferences of decision makers due to problems with assessment methodology and scaling
- ❑ Even in cases where rankings are "correct," these rankings may be reversed by addition of new alternatives.

Case 3: Multi-Criteria Decision Analysis Process

- We used the "Analytical Hierarchy Process"
  - Created criteria hierarchy
  - Military respondents filled out online preference survey
  - Responses used to weight criteria for each respondent
  - Gaps prioritized for each respondent based on weighted criteria
  - Geometric mean across surveys used to produce one ranking for each service
  - Geometric mean across services used to produce one overall ranking

Case 1



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Bioavailability Assessment Program For Hydrophobic Organic Compounds In Sediments

Sediment Contaminant Bioavailability Alliance

Multi-industry alliance to develop an accepted approach that predicts the chemical bioavailability and toxicity of hydrophobic organic compounds in sediment

- Industry-specific case studies
  Standardize new analytical tools with EPA/ASTM
- Support development of regulatory guidance through Interstate Technology Regulatory Council (ITRC) and Federal agencies (EPA/NOAA/USGS)

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Can We Improve Technical Framework for Sediment Management?

Generic ⟷ Site Specific

Look-Up Sediment Screening Value → Chemical Tests to Predict Bioavailability and Toxicity → Directly Measure Bioavailability & Toxicity

Quality of Information

Uncertainty ⟵ ⟶ Confidence

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Value of Improving Chemical Predictors of Sediment Toxicity

- Better information for remedial decision-making
  - *Prioritize where resources are spent*
  - Expedite site closures
  - Reduce costs
- More focused monitoring/assessment methods
  - Residuals following dredging
  - Long-term monitoring of caps
  - MNR evaluation
  - NRDA support

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Sediment Contaminant Bioavailability Program

How Did We Get Here?

- GRI published the "Red Book" - 1996
- Industry & GRI published four major reports 2000 - 2005
- Multiple (~20) scientific peer-reviewed publications since 2001
- Approx. $4 MM in industry R&D on PAH bioavailability in sediments and soils

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Approaches for Assessing Bioavailability

- *Characterize carbon-types and assign carbon-specific partitioning coefficients?*
- Determine sediment pore water chemical concentrations
- Use direct measurements of chemical release to predict bioavailability
- Directly measure uptake and toxicity to organisms directly

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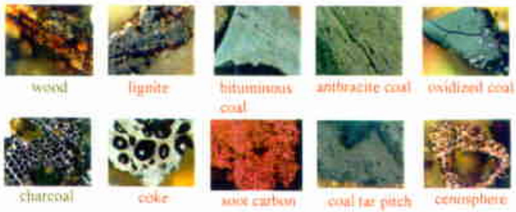
Survey of Hudson River Sediments Demonstrated Presence of Natural and Anthropogenic Carbon



PAH binding (Koc) is very different for different types of carbon

(U. Ghosh et al., 2003)

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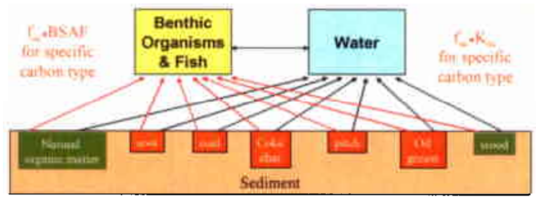
A More Accurate Exposure Model



However, developing partitioning coefficients (BSAF Koc) for individual carbon types is not practical

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Two Chemical Methods have been Developed and Evaluated

- Solid Phase Micro Extraction (SPME)
  - Measures the dissolved concentration of PAHs in sediment pore water
- Supercritical Fluid Extraction (SFE)
  - Measures the release of PAHs in sediment samples

Do these measurements correlate to bioavailability?

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Solid Phase Microextraction (SPME) of Pore Water

Uses sorbent microfiber
Accurately measures PAHs in pore water
Rapid – 30 minutes
Small sample size required
~ 20 ml of sediment
~ 1.5 ml of pore water
Very low detection limit
~ pg/mL (ppt)

(Hawthorne et al., 2005b)

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SPME Detection limits for representative PAHs

	EPA 8270 EQL 1 liter water	SPME 1.5 ml water
Naphthalene (2-ring)	10 μg/l	0.5 μg/l
Phenanthrene (3-ring)	10	0.2
Chrysene (4-ring)	10	0.01
Benzo(a)pyrene (5-ring)	10	0.005
Benzo(g,h,i)perylene (6-ring)	10	0.002

Why is SPME so much more sensitive for larger PAHs?
All molecules collected by SPME are transferred to the GC
For 8270 only ca. 0.1% are injected

(Hawthorne et al., 2005b)

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SPME Fiber Injection into GC/MS

Conventional EPA water analysis methods would require liter(s) of sediment pore water to achieve similar sensitivity

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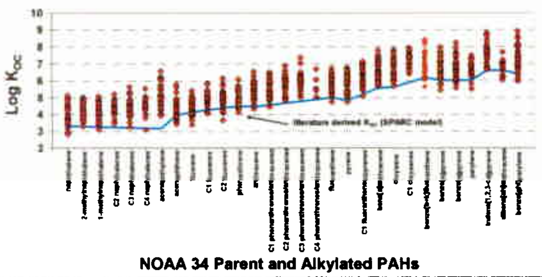
Approximately 10,000 sample specific K_{oc} values have been determined using SPME



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SPME detection limit for PCBs in sediment pore water

- Estimated to be 0.0001 ug/L using 1.5 ml samples*
- Requires method development
- EERC proposal submitted to DOD/SERDP Program for development of SPME (& SFE) to characterize PCB bioavailability in aquatic sediments

*PCB detection limits are estimated based on published SPME partitioning coefficients and electron capture (ECD) response factors reported by the instrument manufacturer.

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Supercritical Fluid Extraction (SFE) of Sediments

- Extraction Conditions
  - Liquid CO_2, 200 atmos, 50°C
  - 40 minutes extraction
- Advantages
  - CO_2 polarity is similar to lipids
  - Release rates correlate to water desorption
  - Solubility of PAHs in CO_2 is proportional to their solubility in water
  - Little effect on OM matrix
  - Can be easily calibrated to biological uptake

(Hawthorne, 2002)

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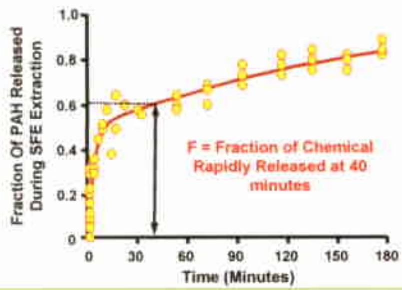
Illustrative SFE Release Curve for PAHs



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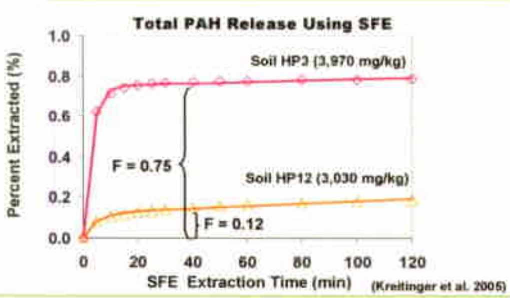
Rapidly Released Fraction (F) can Vary Significantly Between Samples



(Kreitinger et al. 2005)

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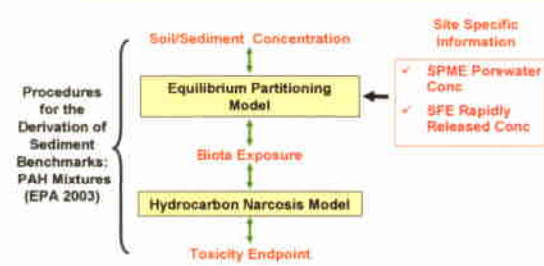
Site Specific Measures Of Chemical Availability Reduce Uncertainty In Predicting Exposure



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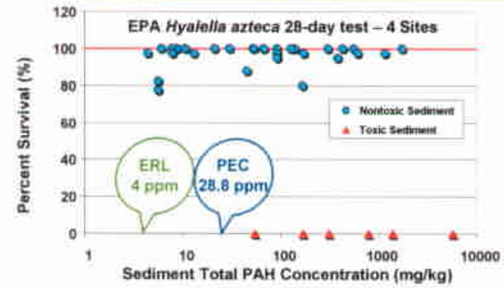
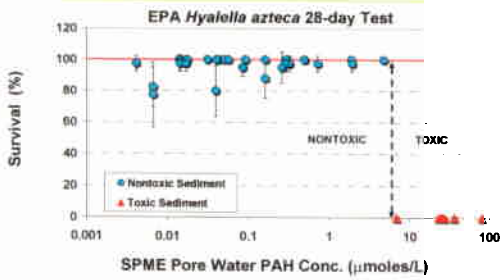
Baseline Field Survey of PAH Bioavailability and Toxicity at MGP sites

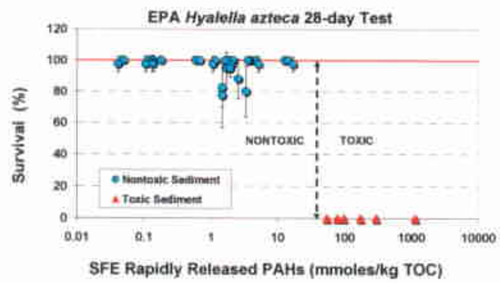
There is No Relationship Between [PAH] and Toxicity



Toxicity to *H. azteca* Can be Predicted by Estimating PAHs in Porewater



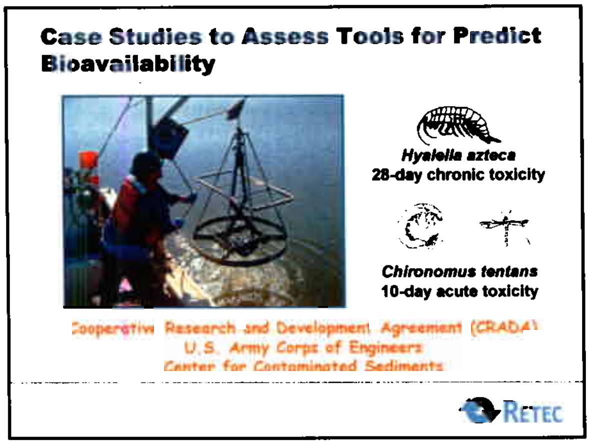
Toxicity to *H. azteca* Can be Predicted by Estimating SFE Rapidly Released PAHs

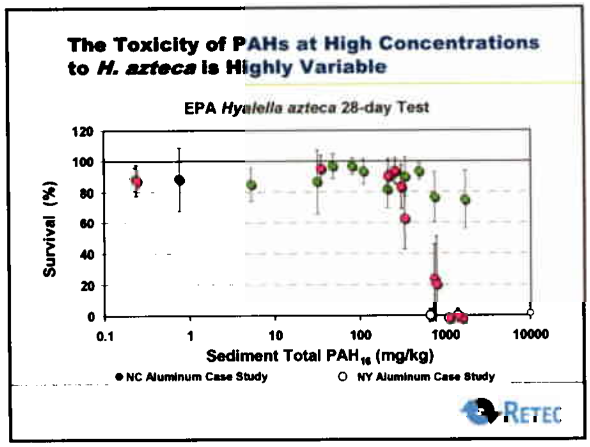


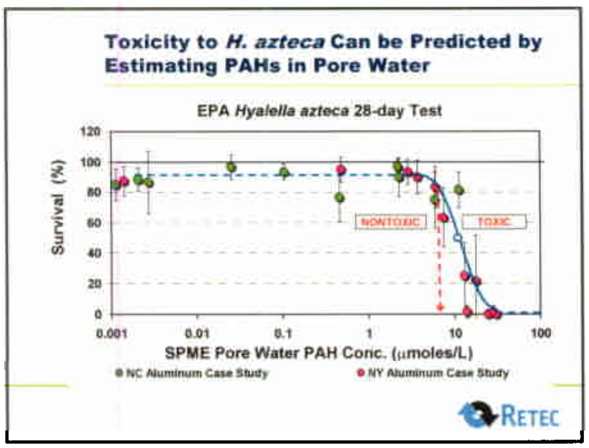
Four Case Study Projects are Being Conducted at Utility and Aluminum Sites

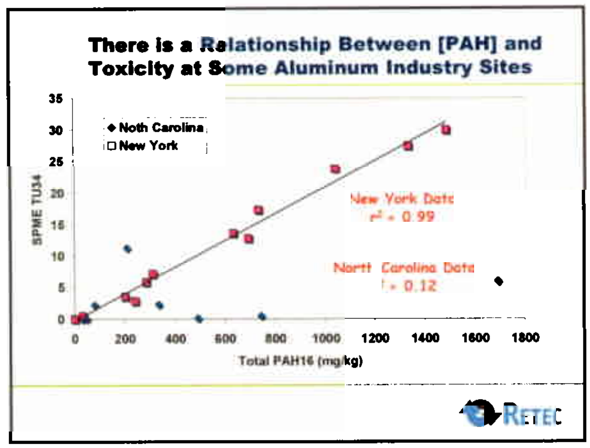
Case Study Goals

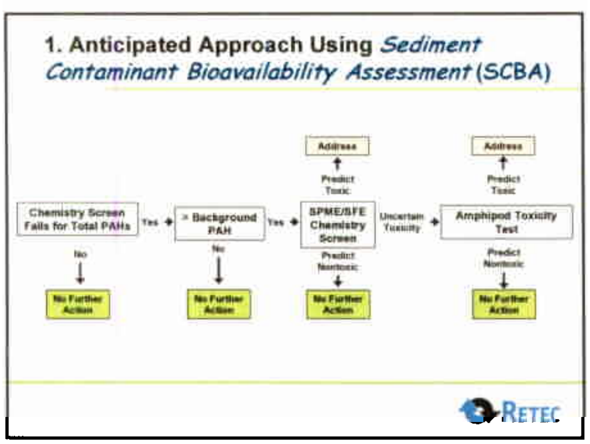
- Determine PAH concentration protective of aquatic life
- Evaluate new chemical tests for predicting bioavailability & toxicity
  - SPME for measuring pore water concentration
  - SFE for measuring rapidly released concentration
- Assess whether sediment mgmt costs can be reduced


Case Studies to Assess Tools for Predict Bioavailability
Hyalella azteca
28-day chronic toxicity
Chironomus tentans
10-day acute toxicity
Cooperative Research and Development Agreement (CRADA)
U.S. Army Corps of Engineers
Center for Contaminated Sediments
RETEC


The Toxicity of PAHs at High Concentrations to H. azteca is Highly Variable
EPA Hyalella azteca 28-day Test
Survival (%)
Sediment Total PAH16 (mg/kg)
NC Aluminum Case Study
NY Aluminum Case Study
RETEC


Toxicity to H. azteca Can be Predicted by Estimating PAHs in Pore Water
EPA Hyalella azteca 28-day Test
Survival (%)
NONTOXIC
TOXIC
SPME Pore Water PAH Conc. (µmoles/L)
NC Aluminum Case Study
NY Aluminum Case Study
RETEC


There is a Relationship Between [PAH] and Toxicity at Some Aluminum Industry Sites
Noth Carolina
New York
SPME TU34
New York Data
r² = 0.99
North Carolina Data
r² = 0.12
Total PAH16 (mg/kg)
RETEC


1. Anticipated Approach Using Sediment Contaminant Bioavailability Assessment (SCBA)
Chemistry Screen Fails for Total PAHs
Yes
> Background PAH
Yes
SPME/SFE Chemistry Screen
Uncertain Toxicity
Amphipod Toxicity Test
Address
Predict Toxic
Predict Nontoxic
No
No Further Action
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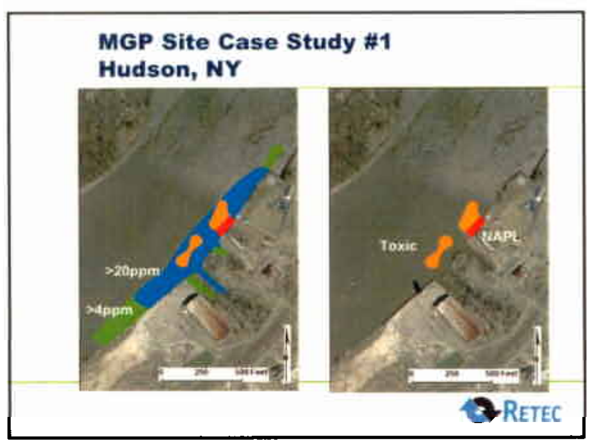
MGP Site Case Study #1
Hudson, NY
>20ppm
>4ppm
Toxic
NAPL
RETEC

Hudson MGP Site
Sediment Remediation Costs

Location	Area (ft²)	Cost (MM)	Net Savings (MM)
DNAPL Impacted	6,100	$2.4	-
Toxic	24,000	$1	-
>20 mg/kg PAH	127,000	$9.1	$9.1
>4 mg/kg PAH	63,000	$4.6	$13.7

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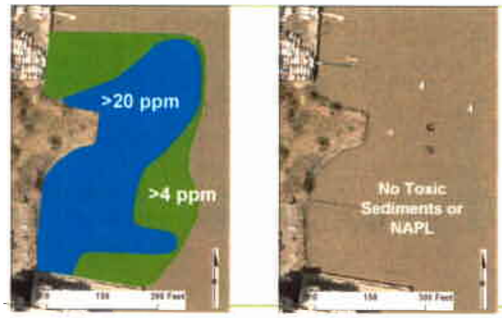
MGP Site Case Study #2
Lower Hudson River



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Lower Hudson River MGP Site
Sediment Remediation Costs

Location	Area (yd²)	Cost (MM)	Net Savings (MM)
DNAPL Impacted	0	$0	-
Toxic	0	$0.3	-
>20 mg/kg PAH	150,000	$11.1	$11.1
>4 mg/kg PAH	99,000	$7.2	$18.3

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Proposed Alliance
Sediment Contaminant Bioavailability Program

Industry Alliance

Program Advisory Board (PAB)

Science Advisory Board (SAB)

Project Manager

Case Studies (Task 1)

Program Support (Tasks 2-5)

Utility Industry
Aluminum Industry
Steel Industry?
Others .....?

2. EPA/ASTM Analytical Method Standardization
3. Technology Transfer
4. Regulatory Guidance Support
5. Alliance Communication & Coordination

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Sediment Contaminant Bioavailability Alliance

Current Members

ALCOA nationalgrid Northeast Gas Association US Army Corps of Engineers

Interested Parties

USS DUPONT DOW conEdison, inc. Central Hudson EDISON ExxonMobil

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Task 1 – Case Studies

- Purpose
  - Short term
    - Site-specific data to expedite closure
    - Provides nationally recognized experts to support work
  - Long term - Data for developing regulatory guidance
- Value
  - Consistent approach
  - Multi-industry sites
  - Multiple contaminant types (PAHs, PCBs, others)
  - Data comparison across industries and sites

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Soil/Sediment Bioavailability Program

Interaction with regulatory agencies is key

- Conduct technical workshops to key State Regulatory Agencies and EPA
  - ✓ New York DEC and DOH
  - ✓ New Jersey DEP
  - ✓ California EPA
- Developed Five-Year Program to Support Integration of Bioavailability Concepts into Federal and State Regulatory Guidance

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Importance of Good Screening Tools To Predict Sediment Toxicity

- Better information for remedial decision-making
  - Prioritize where resources are spent
  - Expedite site closures
  - Reduce costs
- More focused monitoring/assessment methods
  - Residuals following dredging
  - Long-term monitoring of caps
  - MNR evaluation
  - NRDA support

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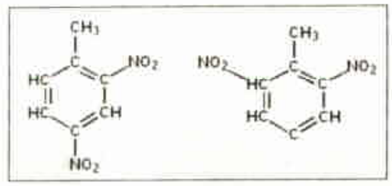
Comparative toxicity of 2,4 and 2,6-DNT in Northern Bobwhite & Integration of parameters to assess reproductive performance

Michael J. Quinn Jr., Ph.D.

2,4 & 2,6 Dinitrotoluene

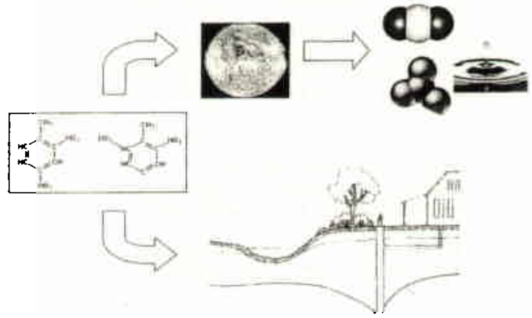


2,4-DNT 2,6-DNT

2,4 & 2,6 Dinitrotoluene

Sources:
- munitions and explosives (122 hazardous waste sites)
- dyes
- elastomers
- polyurethane foams
- coatings

2,4 & 2,6 Dinitrotoluene



2,4 & 2,6 Dinitrotoluene

2,4-DNT
- 13 facilities → 13,590 lbs
  - 2,000 lbs – air emissions
  - 190 lbs – surface water
  - 10,000 lbs – land

2,6-DNT
- 3 facilities → 534 lbs
  - 475 lbs – air emissions
  - 62 lbs – surface water
  - ~0 – land

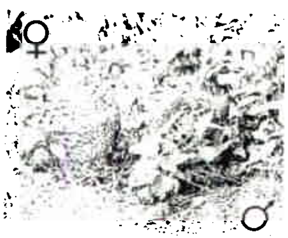
1988 estimates (NSC, 2005)

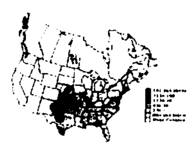
2,4 & 2,6 Dinitrotoluene

Mammalian effects:
- weight loss
- decreased fertility (both sexes)
- anemia
- hepatic effects
- tumors
- neurotoxic effects
- death

Basic Study Design

Subjects: Northern Bobwhite Quail
(*Colinus virginianus*)





Basic Study Design

Exposure: Oral gavage study

Duration: 14-day (subchronic)
60-day (chronic)

Measures:
- **mortality**
- **body weight (weekly)**
- blood chemistry/cellularity
- genomics – development of microarray
- histology – heart, brain, spleen, liver, lungs, kidneys, gonads, GI tract
- **feed consumption**
- **reproduction**

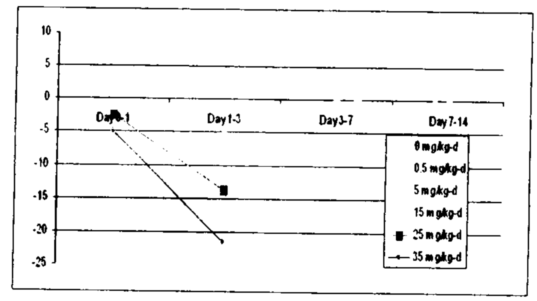
Mortality

	2,4-DNT	2,6-DNT
LD50	55 mg/kg/d	320 mg/kg/d
	19.9-78.6 95% CI	195-479 95% CI
14 d mortality	>25 mg/kg/d	>50 mg/kg/d
60 d mortality	>15 mg/kg/d	>60 mg/kg/d

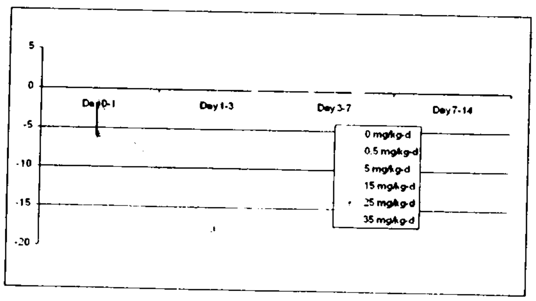
Treatment levels (in corn oil):
2,4-DNT 14 day – 0, 0.5, 5, 15, 25, 35 mg/kg/d
2,4-DNT 60 day – 0, 1, 5, 15, 25, mg/kg/d

2,6-DNT 14 day – 0, 50, 100, 190, 350 mg/kg/d
2,6-DNT 60 day – 0, 5, 10, 40, 60 mg/kg/d

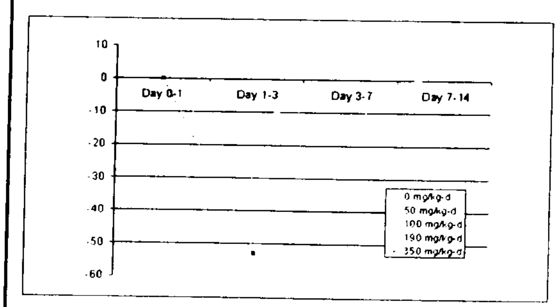
2,4-DNT Male Weight Change
(14 day)



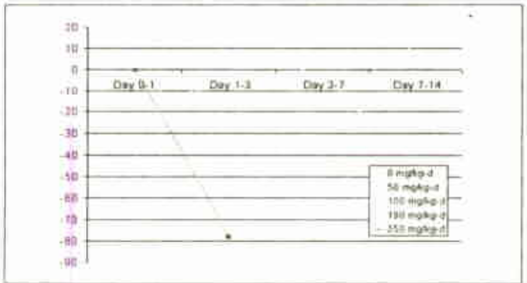
2,4-DNT Female Weight Change
(14 day)



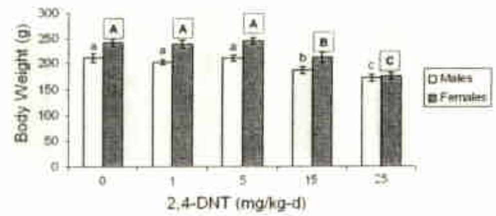
2,6-DNT Male Weight Change
(14 day)



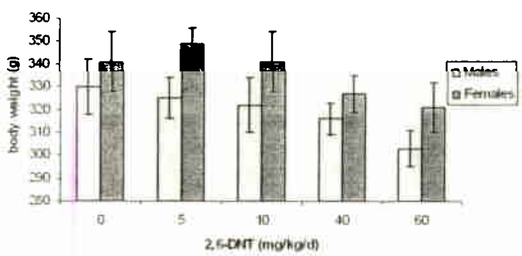
2,6-DNT Female Weight Change
(14 day)



2,4-DNT Final Body Weight
(60 day)



2,6-DNT Final Body Weight
(60 day)

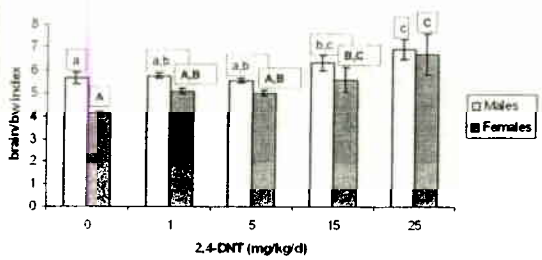


Weights

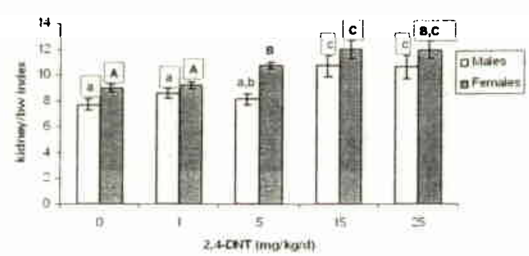
Organ / body weight indices:

- brain
- liver
- kidneys
- spleen
- ovaries
- testes

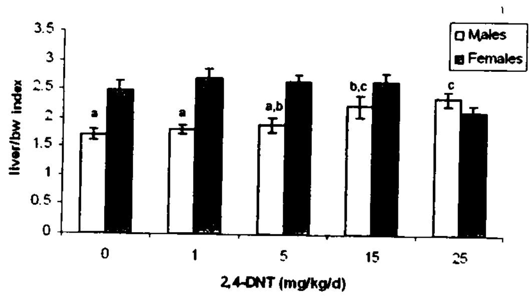
2,4-DNT Brain/BW Index



2,4-DNT Kidney/BW Index

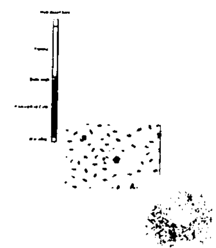


2,4-DNT Liver/BW Index



Hematology / Plasma Chemistry

- hematocrit (PCV)
- erythrocytes
- leukocytes
- hemoglobin
- glucose
- creatine kinase



Hematology / Plasma Chemistry

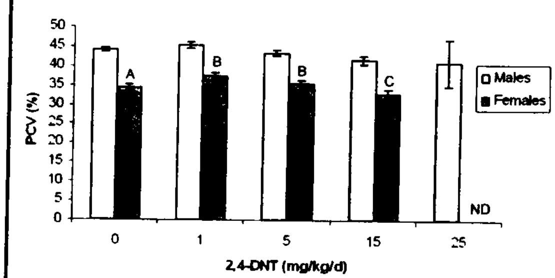
Liver:

- total solids
- total protein
  - albumin
  - globulin
- alkaline phosphatase
- triglycerides
- alanine aminotransferase (ALT)
- aspartate aminotransferase (AST)

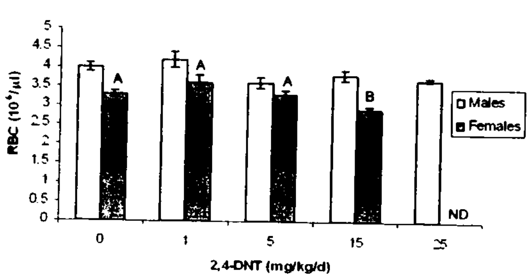
Kidney:

- lactic dehydrogenase
- uric acid
- calcium
- phosphate
- potassium
- sodium
- chloride

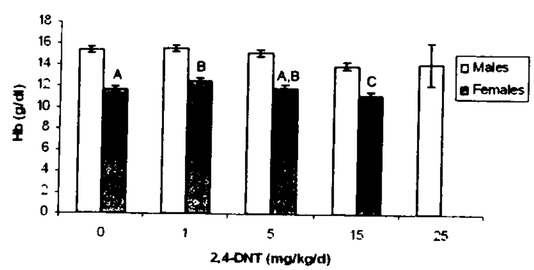
2,4-DNT Packed Cell Volume



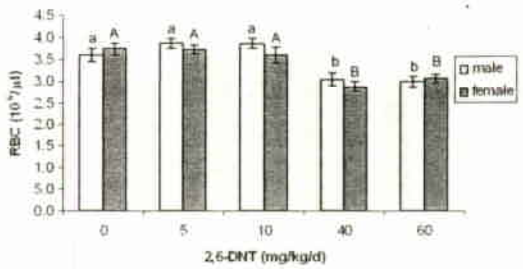
2,4-DNT Red Blood Cells



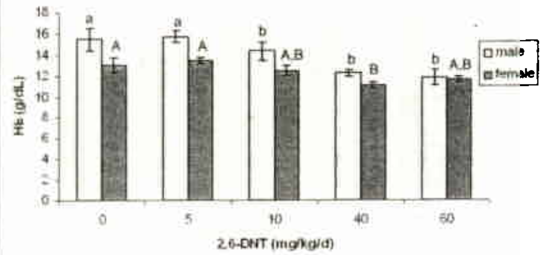
2,4-DNT Hemoglobin



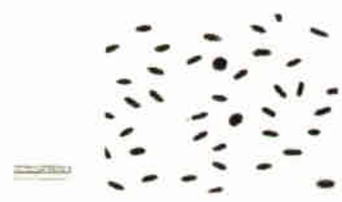
2,6-DNT Red Blood Cells



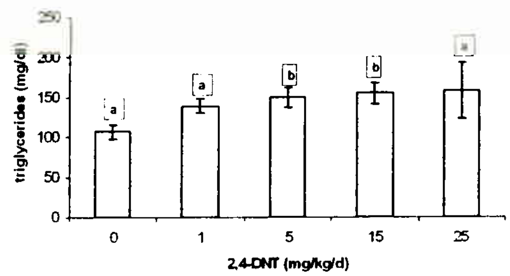
2,6-DNT Hemoglobin



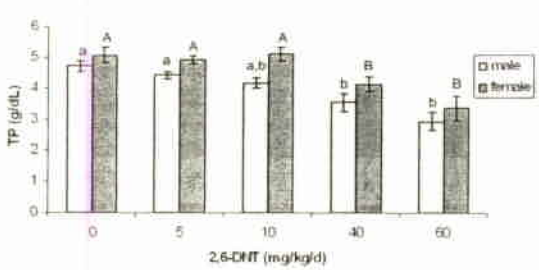
RBC Differences



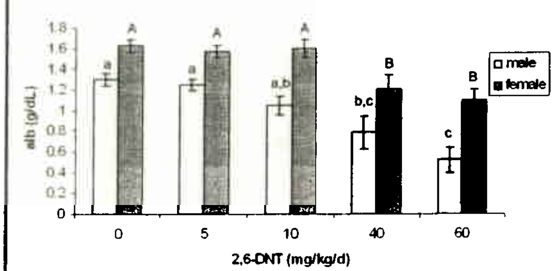
2,4-DNT Triglycerides



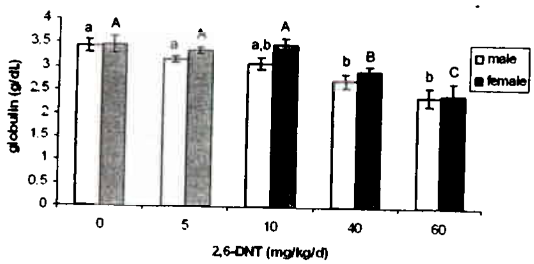
2,6-DNT Total Protein



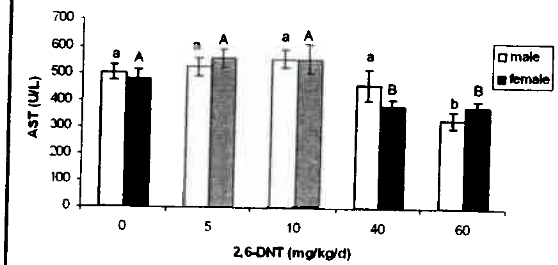
2,6-DNT Albumin



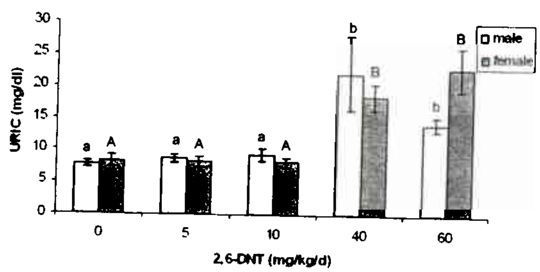
2,6-DNT Globulin



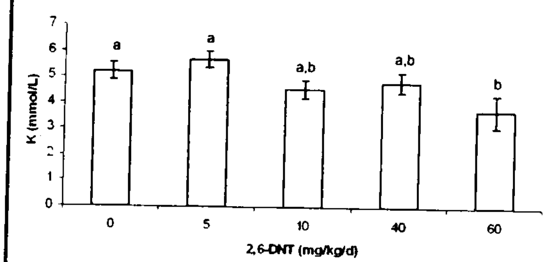
2,6-DNT Aspartate Aminotransferase



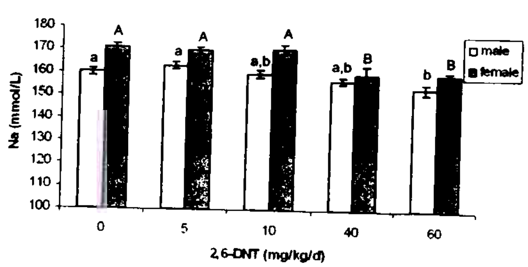
2,6-DNT Uric Acid



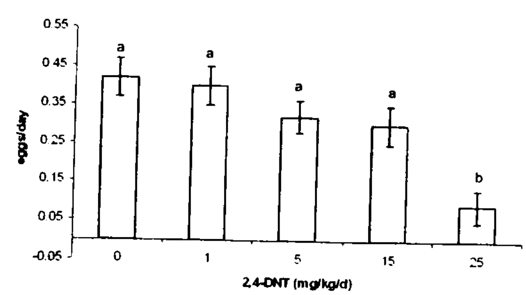
2,6-DNT Potassium



2,6-DNT Sodium



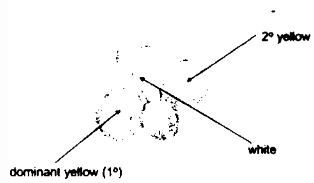
2,4-DNT Egg Production



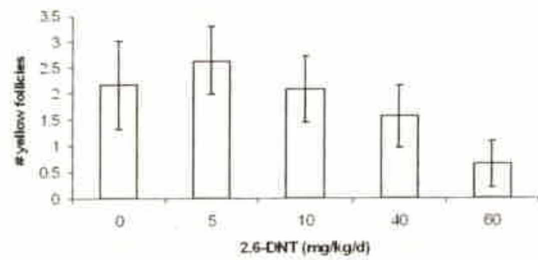
Reproductive Measures

Female:

- follicle hierarchy
- hard egg in tract
- egg laying



Yellow Follicles



Reproductive Measures

Male:

- female introduced into male's cage
- record copulatory behavior
- 3 minutes per trial
- one trial over three days

What is this measuring?

- neuroendocrine development
  - POA / POM
- neuroendocrine activation
  - testosterone → estradiol

Behavioral Measures

Male copulation

- sexual selection
- mounting behavior
  - lag to mount
  - lag to successfully copulate
  - number of mount attempts
  - number of successful cloacal contacts

Behavioral Measures

Only 1 successful copulation in **4** days!

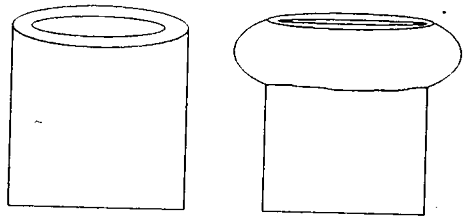
- increased aggression?
- too distracted?
- maturation?
- altered development?

Inappropriate species for tests of reproductive behavior

Consistent Observations

2,4-DNT	2,6-DNT
morbidity prior to death	morbidity prior to death
loose stools	loose stools
increased liver weight	enlarged gall bladder
	green gizzard contents
kidney inflammation	dark, shriveled descending colon & cecae
nephritic urate accumulation (visceral gout)	pale liver & kidneys
	edematous GI tract

Edematous GI Tract



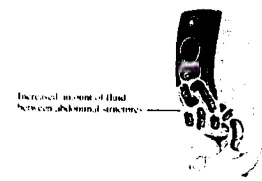
control

2,6-DNT

Edematous GI Tract

Caused by ↓ in serum albumin?

Ascites observed in two birds.



Progression of Feces

Summary of Results

2,4-DNT (Johnson et al., 2005)

LOAEL = 5 mg/kg/d

- **kidney effects** (↑ **plasma uric acid, nephritic accumulation of urates, inflammation**)
- **liver effects** (↑ **triglycerides,** ↑ **liver mass**)

NOAEL = 1 mg/kg/d

2,6-DNT

LOAEL = 40 mg/kg/d

- **loose stools, edema**
  - ↓ **albumin**
- **kidney effects** (↑ uric acid)
- **serum electrolytes** (↓ K & Na)

NOAEL = 10 mg/kg/d

2,6-DNT Maternal Deposition

40 mg/kg/d

albumin = 0.53 µg/g
yolk = 2.86 µg/g

albumin = 0.55 µg/g
yolk = 4.14 µg/g

60 mg/kg/d

albumin = 2.53 µg/g
yolk = 7.75 µg/g

2,6-DNT Maternal Deposition

Future directions:

Analyze additional egg contents

Egg-injection study

- developmental effects
- non-lethal biomarker